


✓ **A MECHANISTIC STUDY OF SOME  
LIGAND SUBSTITUTION REACTIONS OF  
Ni (II) AND Fe (III) COMPLEXES**

**A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of  
DOCTOR OF PHILOSOPHY**

**by**

**H. C. BAJAJ**

**to the  
DEPARTMENT OF CHEMISTRY  
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR  
AUGUST, 1982**



WITH REGARDS  
TO  
MY PARENTS



STATEMENT

I hereby state that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, under the supervision of Professor P.C. Nigam.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been given wherever the work described is based on the findings of other investigators.

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CERTIFICATE I

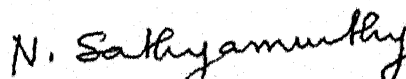
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CERTIFICATE II

Certified that the work contained in this thesis titled,  
"A MECHANISTIC STUDY OF SOME LIGAND SUBSTITUTION REACTIONS OF  
Ni(II) and Fe(III) COMPLEXES" has been carried out by Mr. H.C.  
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ACKNOWLEDGEMENTS

The acknowledgement of gratitude to one's own benefactors is a very difficult task. Words though emphatically expressed may fail to convey the depth of ones genuine feelings. Nevertheless, I would be failing in my duty if I did not place on record my deep sense of gratitude to all eminent scholars, friends and well wishers, who helped me in various ways in the completion of my work.

First of all I wish to express my profound gratitude to Professor P.C. Nigam who was a constant source of inspiration and encouragement to me through his scholarly guidance, constructive suggestions , critical comments and detailed instructions at every stage of my research programme. He has been kind and affectionate to me and has encouraged me during periods of experimental difficulties and emotional disturbances.

I must also express my gratitude to Mrs. Madhuri Nigam for the kind hospitality and affection bestowed on me during my stay in campus.

I am highly grateful to Professors U.C. Agarwala, P.R. Singh S.K. Dogra, N. Sathyamurthy and other teachers, for their kind interest and encouragement from time to time.

I am highly indebted to my research colleagues, Dr. K.Kumar, now at Wayne State University, Detroit, U.S.A. for his kind support during the early period of my research programme, Ms. Madhu Phull, who was a source of inspiration throughout the period of my stay in campus and who offered her helping hand in the preparation of this thesis. I am also indebted to Mr. R.M. Naik and Mr. S.R.Naidu for friendly discussion and maintaining a healthy and cordial atmosphere in the laboratory.

It is my pleasure to thank Mr. Anil Kumar Chaudhary, Mr. B.S. Tomar, Mrs. and Mr. H.C. Srivastava, Mrs. and Mr. B.B. Lohray, Mr. S.B.S. Mishra and Miss Zahida Shirin and other friends for helping me in various matters at different times.

I am also grateful to Dr. A.S. Tyagi of Agra College, Agra, Dr. S.K. Upadhyay of H.B.T.I. Kanpur, Dr. Rajendra Prasad now at Geological Survey of India, Ahmedabad, Shri R.C. Sharma of Govt. College, Kota and Dr. Saroj Prabha of Aeronautical Engg. Department, I.I.T. Kanpur, who contributed their efforts directly and indirectly towards completion of my work.

I thank Messers R.K. Sharma, T.G. Rao and Bakshish Singh for technical assistance, M.D. Pandey and L.P. Tripathi for procuring chemicals and Gauri Singh for preparing drawings. The help provided by Mr. K.K. Bajpai, Mr. R.D. Singh and Mr. M.L. Sharma chemistry office and Mr. M.S. Bhandari of Account Section is sincerely acknowledged.

I finally thank Mr. Anil Kumar for typing this thesis with care and neatness, Mr. B.N. Shukla for cyclostyling and Mr. Dalip for zeroxing the figures.

I also take the opportunity to thank the authorities of the I.I.T. Kanpur and C.S.I.R. New Delhi, for the financial assistance provide for these investigations.

I find myself at a loss for words in expressing my heart felt gratitude to my adored parents and other members of family who bore many hardships in order to support me during my educational career.

Kanpur  
August 1982

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## PREFACE

Transition metal ion complexes have been widely studied to understand the basic processes of coordination chemistry viz. formation, dissociation, exchange and hydrolysis etc. Nickel(II) stands in about the same relation to labile complexes as Co(III) does to inert complexes. The study of Nickel(II) complexes has played an important role in understanding the replacement mechanisms. There is no interference from oxidation or reduction and nickel is the least reactive amongst metals forming labile complexes due to its  $d^8$  configuration. Replacement of bidentate or polydentate ligands from the coordination sphere of nickel(II) by other multidentate or monodentate ligands and effect of presence of other ions viz.  $[H^+]$  or  $[OH^-]$  and effect of temperature on the lability of outgoing ligand provides good insight into the elementary steps of exchange reactions. Some binuclear complexes, where metal atoms are linked through ligand bridges also offer interesting opportunity to understand their dissociation behaviour and the effect of nature and stereochemical disposition of ligands on their dissociation rates.

The thesis consists of seven chapters of which the first is introductory and the following four are devoted to the various investigations carried out on the ligand substitution reactions of some mono, bis and binuclear complexes of Nickel(II) with aminocarboxylates and polyamines.

The sixth chapter describes extension of these studies to the reaction of ethylenediamine tetraacetato(hydroxo)-ferrate(III) ion with cyanide ion. The seventh chapter gives

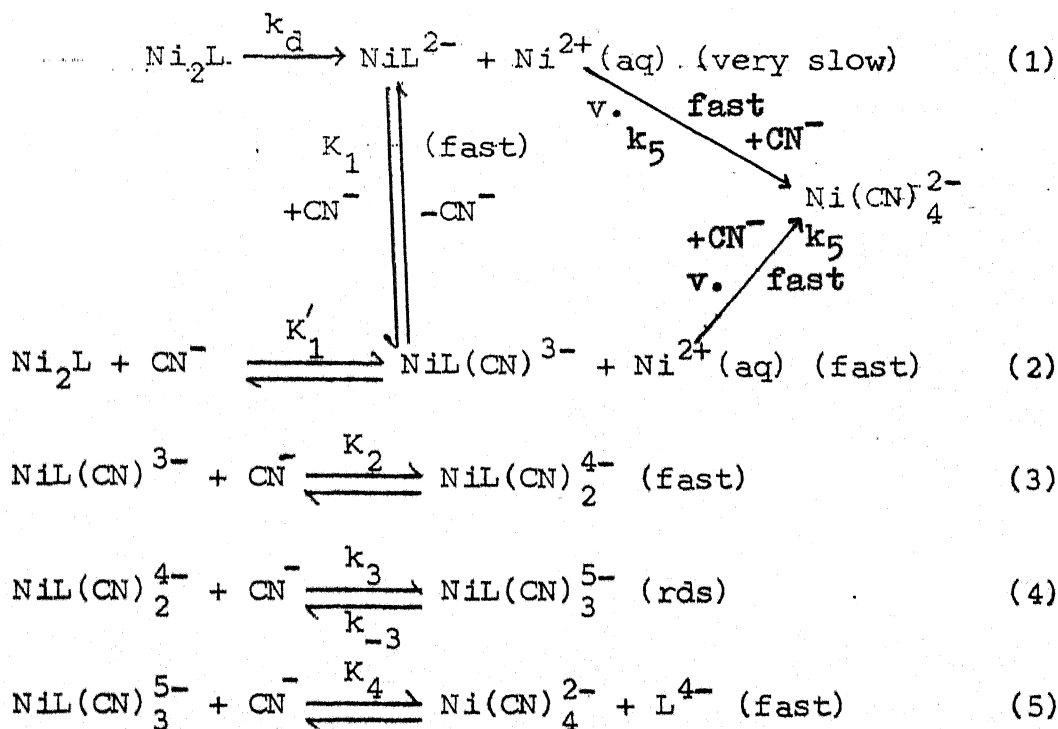


a summary of the work and the scope for the further investigations.

The first chapter is introductory. It gives a critical review of the current knowledge about ligand substitution reactions of metal complexes in general and nickel complexes in particular. Some space is devoted to formation and dissociation of ternary complexes and also to solvent effects.

The second chapter deals with the reaction behaviour of binuclear nickel(II) complex viz  $\text{Ni}_2\text{EGTA}$  with cyanide ion. Although a considerable amount of data is now available on the reaction of mono(aminocarboxylato)nickel(II) complexes but binuclear complexes of nickel(II) have attracted little attention in kinetic studies. The conditions used for this reaction were  $\text{pH} = 11.0 \pm 0.1$ ,  $I = 0.1\text{M}$  and  $\text{temp.} = 25^\circ\text{C}$ . The forward reaction was carried out in presence of large excess of cyanide ions. A plot of  $\log$  (rate constant) vs  $\log [\text{CN}]_T$  showed a zero order dependence in cyanide at low concentrations while a first order dependence at higher concentration level of cyanide. The backward reaction is first order in  $\text{Ni}(\text{CN})_4^{2-}$  as well as in EGTA and inverse first order in free cyanide. On the basis of experimental observations it was inferred that the initial part of the forward reaction proceeds by two paths, first a slow dissociation of  $\text{Ni}_2\text{L}$  to give  $\text{NiL}$  and  $\text{Ni}_{(\text{aq})}^{2+}$  and a fast cyanide assisted dissociation of  $\text{Ni}_2\text{L}$  to give  $\text{NiL}(\text{CN})_x$  and  $\text{Ni}_{(\text{aq})}^{2+}$  ( $x=2$ ). The subsequent steps are the same as for reactions of mononuclear complexes with

cyanide. The over all mechanistic scheme can be represented as



The activation parameters nicely support this mechanism.

An analysis of the pH dependence of forward rate makes it possible to resolve the rate constants due to  $\text{CN}^-$  and  $\text{HCN}$  which is also a reactant below pH 9. A correlation between the dissociation rate constants  $k_d^{\text{Ni}_2\text{L}}$  and the overall stability constants  $\beta_{\text{Ni}_2\text{L}}$  has been attempted, where L is TTHA, DTPA and EGTA.

The results of the reaction between bis complexes of nickel,  $\text{NiL}_2$  (where L is diethylene triamine or ethylene diamine), with cyanide ion form the subject matter of chapter three. The bis complexes are not converted directly to  $\text{Ni}(\text{CN})_4^{2-}$ , but first lose one ligand molecule and cyanide ion assists this loss. The

mechanism of later part of reaction is same as for reactions of mononuclear complexes with cyanide. The temperature dependence studies support this hypothesis and pH effect suggests that HCN is also a reactant below pH 9.

In the fourth chapter of the thesis results of kinetics of formation of aminocarboxylato nickel(II) from Ni(trien) chelate are presented, where aminocarboxylates used are HEEDTA (hydroxy-ethyl-ethylene diamine triacetic acid) and DTPA (Diethylene-triamine penta acetic acid). The reaction was followed by the cyanide quenching method. The conditions of experiment were same as given in chapters 2 and 3. The reaction is first order each in  $\text{Ni}(\text{Trien})^{2+}$  and in  $\text{L}^{n-}$  (HEEDTA or DTPA) and is found to be strongly dependent upon hydrogen ion concentration. The rate of reaction first decreases with an increase of pH, passes through a minimum at pH 8 and again increases. This behaviour has been explained on the basis of reactivities of protonated and hydroxo species of Ni Trien and protonated forms of  $\text{L}^{n-}$ . A ten step reaction mechanism has been proposed consistent with the experimental observations and the rate determining step has been identified.

The fifth chapter deals with the kinetics of ligand substitution reactions of polyamine nickel(II) chelates with Par, 4-(2-Pyridyl azo)resorinol, where polyamines used are triethylenetetraamine (Trien) and tetraethylenepentamine(Tet) utilising stopped flow and other UV-Vis spectrophotometers. The

nickel (Polyamine) chelate reacts rapidly with Par to finally produce  $\text{Ni}(\text{Par})_2$ . But two distinct steps are observed in this reaction. The first step is first order with respect to both  $\text{Ni}(\text{Polyamine})$  and Par, which shows the formation of a ternary complex,  $\text{Ni}(\text{Polyamine})(\text{Par})$  in this step. The second step is first order in the ternary complex and is independent of Par concentration. This indicates the dissociation of the ternary complex prior to formation of  $\text{Ni}(\text{Par})_2$ . The effects of pH and temperature on both reaction steps have been investigated and used to support the proposed mechanism.

In the sixth chapter, the kinetics of reaction of ethylenediaminetetra acetato (hydroxo) ferrate(III),  $\text{FeY}(\text{OH})^{2-}$ , with cyanide ion is presented. This reaction consists of three stages. The first involves the formation of  $\text{Fe}(\text{CN})_5(\text{OH})^{3-}$ , the second is conversion of  $\text{Fe}(\text{CN})_5(\text{OH})^{3-}$  to  $\text{Fe}(\text{CN})_6^{3-}$  and finally the reduction of  $\text{Fe}(\text{CN})_6^{3-}$  to  $\text{Fe}(\text{CN})_6^{4-}$  due to oxidation of EDTA, released within the system, by  $\text{Fe}(\text{CN})_6^{3-}$  formed in the system. The first stage shows a variable order dependence in cyanide, ranging from one at higher cyanide concentration to three at lower cyanide concentration. The backward reaction i.e., the reaction between  $\text{Fe}(\text{CN})_5(\text{OH})^{3-}$  and EDTA is first order in each reactant and inverse first order in free cyanide. These results lead to a five step mechanism for the formation of  $\text{Fe}(\text{CN})_5(\text{OH})^{3-}$  from  $\text{Fe}(\text{EDTA})(\text{OH})$  complex. The second stage shows first order dependence each in  $\text{Fe}(\text{CN})_5(\text{OH})^{3-}$  and cyanide. The third stage

follows second order kinetics and is strongly dependent on hydroxide concentration as well. A general mechanism consistent with all kinetic data is proposed. The seventh and last chapter gives a summary of work and scope for further investigations.

The thesis contains figures, tables and references wherever needed.

While particular care has been taken to give due credit to the work reported by other authors in the literature, the author begs to be excused for purely unintentional omissions, if any, due to oversight and for errors which could be traced herein.

List of Abbreviations

Asp	Aspartic acid
ATP	Adenosine triphosphate
bipy	2,2'-Bipyridyl
bn	Butanediamine
CDTA	Cyclohexanediamine tetra-acetic acid
dacco	1,5-diazacyclooctane
Dien	Diethylenetriamine
N,N'-di-meen	N,N'-Dimethylethylenediamine
DMF	Dimethyl formamide
DMSO	Dimethyl sulphoxide
dto	Dithiooxalate
DTPA	Diethylenetriamine penta-acetic acid
EDDA	Ethylenediamine diacetic acid
EDMA	Ethylene diamine mono-acetic acid
EDTA	Ethylene diamine tetra-acetic acid
EGTA	(Ethylene dioxy) diethylene dinitrilo-tetra-acetic acid
en	Ethylenediamine
EtOH	Ethanol
GEDTA	2,2'-Ethylenedioxy bis(ethyliminodiacetic acid)
gly	glycine
HEDTA	N-(2-hydroxy ethyl)ethylenediaminetetraacetic acid
HEEDTA	(Hydroxy ethyl) ethylenediamine triacetic acid

HEIDA	(Hydroxy ethyl) iminodiacetic acid
IDA	Iminodiacetic acid
MeCN	Acetonitrile
MeOH	Methanol
$\alpha$ N $\beta$ N	$\alpha$ -Nitroso $\beta$ -Naphthol
$\alpha$ N $\beta$ N-3-SO <sub>3</sub>	$\alpha$ -Nitroso $\beta$ -Naphthol-3-sulphite
$\alpha$ N $\beta$ N-3-6-SO <sub>3</sub>	$\alpha$ -Nitroso $\beta$ -Naphthol-3,6-disulphite
NSA	Nitrosalicylic acid
NTA	Nitrilo triacetic acid
Pada	Pyridine-2-azo-p-dimethylaniline
Par	4-(2-Pyridylazo)resorcinol
1,10 Phen	1,10 Phenanthroline
Pent	Penta ethylene heptamine
Py	Pyridine
TG/Trigly	Triglycine
Terpy	Terpyridyl
Tetren/Tet	Tetraethylene pentaamine
Tetmeen	Tetramethyl ethylene diamine
Tmen	Trimethylene diammonium ion
TTHA	Triethylene tetraamine hexaacetic acid
Tren	2,2',2''-triaminotriethylamine
Trien	Triethylene tetramine
Trimeen	Trimethylene ethylenediamine
TP	Polytriphosphate

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## CHAPTER I

### GENERAL INTRODUCTION

#### I.1 Scope and Purpose of Work

The study of mechanisms of chemical reactions, employing reaction kinetic data, has been a subject of interest for several chemists. Such investigations provide valuable clues for understanding the salient electronic, structural and stereochemical features of a chemical process at the molecular level. For a chemist the importance of kinetic study lies in the fact that by understanding the dependence of rates on the reaction variables viz. concentration, temperature, pressure and solvent etc, one can control the course of a reaction. Thus the conditions required for favouring formation of desired product(s) can be successfully worked out.

The substitution process permeates the whole realm of coordination chemistry. It is not infrequently the first step in a redox process<sup>1-3</sup> or in a dimerization or a polymerization reaction<sup>4</sup>. An understanding of the kinetics of substitution can

be important for defining the best conditions for a preparative or analytical procedure in coordination chemistry<sup>5</sup>. The process is undoubtedly important in the reactions of metal or metal activated enzymes, for example in the inhibition of the catalytic function of metalloenzymes<sup>6</sup> by ligands and the transport of metal ions through cell membranes<sup>7</sup>.

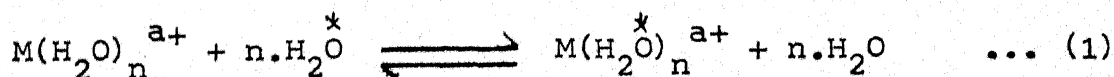
Most of the early kinetic studies of substitution were concerned with the inert Co(II) complexes which Werner had so well characterized and which underwent reactions at conveniently measurable rates. An earlier review by Taube<sup>8</sup> draws attention to the wider world of labile octahedral complexes of transition metals and to reactions which were complete within mixing time. The collection of quantitative data for a large number of rapidly reacting bivalent and tetravalent transition metal complexes of the Vanadium-Zinc group had to await the development of flow methods as well as the invention of relaxation techniques<sup>9</sup>.

In the past few years several excellent monographs on the mechanisms of inorganic reactions have appeared<sup>10-16</sup> and a significant drive has been made towards visualising the nature of a variety of intermediates and transition states. Lately reactions of coordination compounds have been investigated to test various theories of chemical reactivity. For example, the base hydrolysis of penta-amine cobalt(III) ion has been used to study the effect of hydrostatic pressure<sup>17</sup>, ionic strength<sup>18</sup> and ion pairing<sup>19</sup> on the reaction rates. Many metal ions are known to act as catalysts

in organic and biological systems. Their reactivities may form the basis for better understanding, for example, of the striking difference between otherwise similar  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as enzyme activators<sup>20</sup>.

Many possibilities of analytical interest<sup>21-27</sup> are provided by the study of coordination reactions (mainly ligand substitution reactions). Differential determination of metal ions has become possible by the use of differences in the rates for the forward or reverse reactions of different metal ions<sup>28-32</sup> with judiciously chosen ligands. The concentration of  $\text{Hg}^{2+}$  has been determined upto  $10^{-7}\text{M}$  level by its catalytic effect on the substitution reaction of cyanide in hexacyanoferrate(II) by p-nitrosodiphenylamine<sup>27</sup>. Similarly Trien<sup>24</sup> and Triglycine<sup>25</sup> have been estimated at  $10^{-5}\text{M}$  concentration level by a kinetic method. It may be emphasized here that a detailed kinetic picture of a reaction is quite often a necessary prerequisite for its use for analytical purpose.

One of the most reliable methods for assigning the solvation number of metal ions involves exchange studies in reactions of the type



Provided the rate of exchange is measurable, and the flow methods or NMR<sup>33</sup> spectroscopy can help to attain this, the value of n can be determined. The hexa coordinated structure for  $\text{Al}(\text{H}_2\text{O})_6^{3+}$

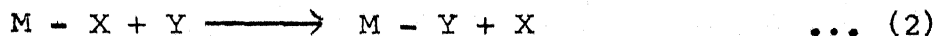
and  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  in water<sup>34,35</sup>, as well as for  $\text{Co}(\text{NH}_3)_6^{3+}$  in liquid ammonia<sup>36</sup> have been deduced by solvent exchange kinetics.

Some ligand exchange data have been used to calculate the stability constants of mixed ligand complexes<sup>37-45</sup>, which is otherwise difficult to calculate by usual procedures because of their transient existence or extremely small concentration in which they are produced as intermediates in multistep reactions. The rate data of ligand exchange reactions involving a four step reaction between aminocarboxylatonickel(II) and cyanide ion have been used to calculate the stability constants<sup>41-45</sup> of mixed-ligand complexes of the type  $\text{NiL}(\text{CN})_x^{2-n-x}$ , where  $\text{L}^{n-}$  is an amino-carboxylate or polyamine. The stability constants of complexes of alkali metals with aminocarboxylates have also been determined by using the rate data of exchange reactions of aminocarboxylates with  $\text{Ni}(\text{CN})_4^{2-}$  by studying the effect of concentration of these alkali metal ions on the above stated reaction<sup>46</sup>.

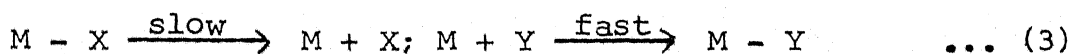
The study of kinetics of reactions of nickel(II) complexes has played an important role in enhancing our understanding of replacement mechanisms. The present work was started with the object of obtaining a better understanding of the ligand exchange processes in general and polydentate ligand displacement or exchange on nickel(II) and iron(III) in particular.

## I.2 Classification of Substitution Reactions

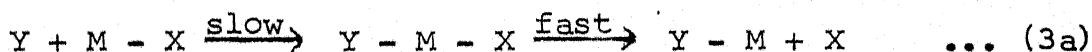
For a ligand substitution process



two distinctly different types of mechanisms are possible



A process where rupture of the metal-ligand (eg. M-X) bond is primarily important in the transition state is called  $S_N1$  according to Ingold's notation<sup>47</sup> or Dissociative process, 'D', according to Langford and Gray's terminology<sup>48</sup>. Alternatively, formation of the M - Y bond may be primarily important in the transition state without any significant rupture of the M-X bond.



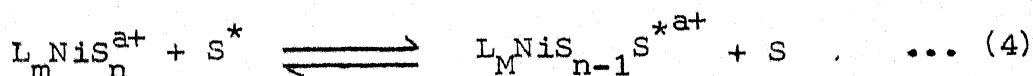
This is a bimolecular nucleophilic substitution process designated as  $S_N2$  by Ingold<sup>47</sup> and an Associative process, 'A', according to Langford and Gray<sup>48</sup>. However, 'D' and 'A' processes are limiting situations and in many systems there may be different degrees of M-X bond rupture and M-Y bond formation in the transition state. These have been termed as Interchange process or 'I' process by Langford and Gray<sup>48</sup>. An interchange process can be further sub classified as Associative interchange process, ' $I_a$ ' and Dissociative interchange process, ' $I_d$ '.

### I.3 Literature Survey

The octahedral complexes of metals have been subjected to a great deal of kinetic investigations. A brief survey of the significant developments in this field will be reported here though the discussion will be mainly centred around the octahedral complexes of nickel(II) as an illustrative example.

#### I.3.1 Ligand exchange reactions:

Solvent exchange is perhaps the most important example of this kind of reaction



where L represents a ligand and S the solvent molecules. The kinetics of this kind of reactions have been studied both in pure solvent and in mixtures of coordinating and non-coordinating solvents.

Exchange in pure solvents has been found to obey a first order rate law

$$\text{Rate} = nk_{\text{ex}} [L_m NiS_n^{a+}] \quad \dots (5)$$

where n is the number of molecules of solvent present in the complex and  $k_{\text{ex}}$  is the specific rate for the exchange of a single molecule of that solvent. Some kinetic data for the solvent exchange of  $NiS_6^{2+}$  complexes (S = solvent) are given in Table I.1.

Table I.1 Kinetic data for the solvent exchange of some octahedral nickel(II) complexes in pure solvent at 25°C

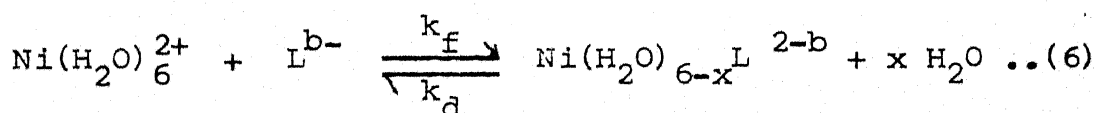
Complex	$k_{\text{ex}}, \text{sec}^{-1}$	$\Delta H_{\text{ex}}^\ddagger$ kcal mole <sup>-1</sup>	$\Delta S_{\text{ex}}^\ddagger$ eu	Ref.
$\text{Ni}(\text{H}_2\text{O})_6^{2+}$	$4.4 \times 10^4$	10.3	-5.2	49
	$3.6 \times 10^4$	12.3	+3.6	50
	$3.0 \times 10^4$	10.8	-1.7	51
	$2.7 \times 10^4$	11.6	+0.6	52
$\text{Ni}(\text{MeOH})_6^{2+}$	$1.0 \times 10^3$	15.8	+8	53
$\text{Ni}(\text{EtOH})_6^{2+}$	$1.1 \times 10^4$	10.8	-4	54
$\text{Ni}(\text{NH}_3)_6^{2+}$	$1.0 \times 10^5$	9.9	-2	55
	$0.47 \times 10^5$	10.0	-3	56
$\text{Ni}(\text{DMF})_6^{2+}$	$6.9 \times 10^3$	14.6	+6	57
	$3.8 \times 10^3$	15.0	+8	58
$\text{Ni}(\text{MeCN})_6^{2+}$	$12.4 \times 10^3$	11.8	-0.2	59
	$3.9 \times 10^3$	10.9	-8.8	60
	$2.8 \times 10^3$	11.7	-3.6	61
$\text{Ni}(\text{DMSO})_6^{2+}$	$9.3 \times 10^3$	7.3	-16	62
	$7.5 \times 10^3$	8.0	-16	63
	$5.2 \times 10^3$	12.1	-1.3	64
	$3.2 \times 10^3$	13.0	-1.4	65



The data reported in Table I.1 show that the enthalpies and entropies of activation are largely dependent on the exchanging solvent, although little effect is observed at 25°C on the exchange rate constant,  $k_{ex}$ . Several factors are believed to contribute to the solvent effect. Among these, the most important are: (i) the metal-ligand bond energies; (ii) the ability of the ligands to provide electronic stabilization for an intermediate state; (iii) the steric requirements of the different ligands; (iv) the solvation difference between ground and transition state and (v) the structural properties of the solvent<sup>66,67</sup>.

### I.3.2 Formation Reactions of Nickel(II) Complexes:

The kinetics of formation reactions represented by Eqn.(6) are among the most thoroughly investigated ones in the chemistry



of octahedral complexes of Ni(II). The rate law obeyed by these reactions has the general form;

$$\text{Rate} = k_f [\text{Ni}(\text{H}_2\text{O})_6^{2+}] [\text{L}^{b-}] - k_d [\text{Ni}(\text{H}_2\text{O})_{6-x}\text{L}^{2-b}] \quad \text{..(7)}$$

The second term in the above Eqn (7) represents the dissociation

rate. The observed pseudo first order rate constant for the complex formation is

$$k_{\text{obsd}} = k_f [L^{b-}] \quad \dots(8)$$

The second order formation rate constants for the replacement of  $H_2O$  by a variety of unidentate ligands, according to equation (6) are given in Table I.2.

Table I.2. Rate Constants for formation ( $k_f$ ) of nickel(II) complexes with some unidentate ligands at  $25^\circ\text{C}$ .

Ligand	$10^{-3} \times k_f^{a,c}$ lit mole <sup>-1</sup> sec <sup>-1</sup>	$10^{-4} \times k_o^{b,c}$ sec <sup>-1</sup>	Ref.
$NH_3$	4.6	3.0	68
Py	4.0	3.0	69
imidazole	5.0	1.6	70
$SCN^-$	6.0	0.6	71
$HC_2O_4^-$	5.0	0.3	72
$CH_3PO_4^{2-}$	280	0.7	73
$SO_4^{2-}$	-	1.5	74
$F^-$	8.0	0.8	75
$H_2O$	-	3.0	51

a  $k_f = K_{OS} k_o$

b.  $k_o = k_f / K_{OS}$

c. Vide supra, Eqn. (9)

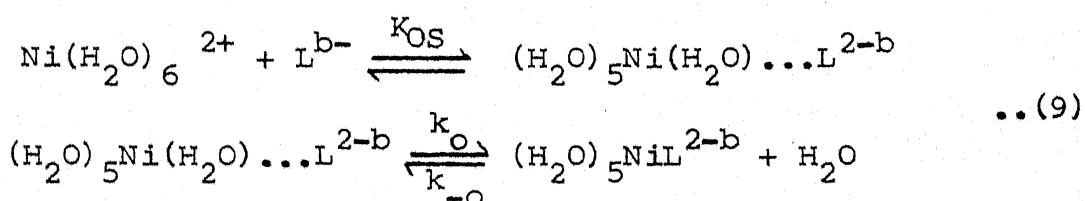
The roughly constant values of  $k_f$ , provided the entering ligands bear the same charge, suggest that this behavior is consistent with the dissociative mechanism in which the entering ligand plays a relatively minor role in the rate determining loss of a molecule of solvent. The occurrence of a dissociative mechanism is also consistent with the values of volume of activation ( $7-12 \text{ ml mole}^{-1}$ ) for the reaction of nickel(II) ion with some uncharged ligands in water<sup>76</sup> (Table I.3).

Table I.3. Volumes of Activation ( $\Delta V^\ddagger$ ) for the reaction of nickel(II) ion with some uncharged ligands.

Ligand	Temp.	$\Delta V^\ddagger (\text{cm}^3 \text{ mole}^{-1})$	Ref.
$\text{NH}_3$	$30^\circ\text{C}$	$7.1 \pm 1.0$	76
Pada*	$49^\circ\text{C}$	$8.2 \pm 0.1$	76,77
glycinate	-	$8.0 \pm 2.0$	78
imidazole	$25^\circ\text{C}$	$11.0 \pm 1.6$	79
murexide	$25^\circ\text{C}$	$12.2 \pm 1.5$	79

\* Pada is Pyridine-2-azo-p-dimethylaniline

The generally accepted mechanism of complex formation was originally proposed by Eigen and Tamm<sup>80-83</sup>. It involves the preliminary diffusion controlled formation of an outer-sphere complex between nickel(II) and the incoming ligand. The rate-determining step of the overall process is the loss of a solvent molecule from the first coordination layer of this outer sphere complex(Eqn. 9).



where  $K_{\text{OS}}$  is the equilibrium constant for the formation of the outer-sphere complex,  $k_o$  is the rate constant for the loss of a solvent molecule from the outer-sphere complex and  $k_{-o}$  is the rate constant for the reverse process.

According to Eigen mechanism, the rate constant for the complex formation,  $k_f$ , is given by

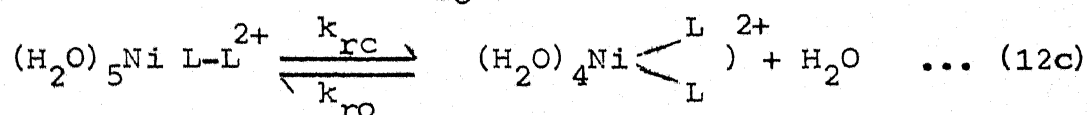
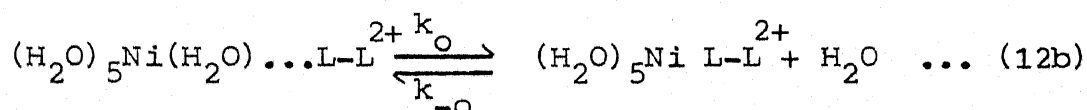
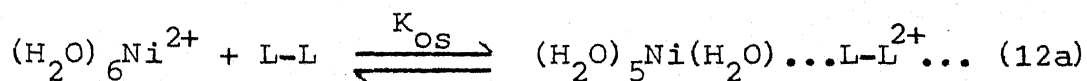
$$k_f = \frac{k_o K_{\text{OS}}}{1 + K_{\text{OS}} [\text{L}^{b-}]} \quad \dots (10)$$

which becomes

$$k_f = k_o K_{\text{OS}} \quad \dots (11)$$

when  $K_{\text{OS}} [\text{L}^{b-}] \ll 1$ .

When the entering ligand is bidentate, we can still extend the Eigen mechanism<sup>80</sup> to the formation of monochelates according to equations 12a - 12c, where the bidentate ligand is represented by L-L.



In Eqn. (12c),  $k_{rc}$  and  $k_{ro}$  are the rate constants for ring closure and ring opening steps respectively. According to this mechanism, the specific rate constant for complex formation,  $k_f$ , is given by

$$k_f = \frac{K_{\text{os}} k_o k_{rc}}{k_{-o} + k_{rc}} \dots (13)$$

If  $k_{rc} \gg k_{-o}$  i.e., if ring closure is a fast step, then  $k_f = K_{\text{os}} \cdot k_o$ , equivalent to equation (11). The overall rate of chelate formation will then be determined by the rate of formation of  $\text{NiL-L}$  species and will be governed by factors applicable to unidentate ligands. However, if  $k_{rc} \ll k_{-o}$  i.e., if ring closure is rate determining, then

$$k_f = K_{\text{os}} \frac{k_o \cdot k_{rc}}{k_{-o}} = K_{\text{os}} K_1 k_{rc} \dots (14)$$

where  $K_1 = k_o/k_{-o}$ . Some values of  $k_f$ , for the formation of  $\text{NiL}(\text{H}_2\text{O})_n$  complexes for bidentate and multidentate ligands are summarised in Table I.4.

Table I.4. Specific rate constant,  $k_f$ , for the formation of  $\text{NiL}(\text{H}_2\text{O})_n$  complexes with some bidentate and multidentate ligands at  $25^\circ\text{C}$ .

Ligand	$10^{-3}, k_f, \text{M}^{-1}\text{s}^{-1}$	$10^{-4} k_o$	Ref.
$\text{H}_3\text{Tet}^{3+}$	3.5	-	84
$\text{H}_3\text{Pent}^{3+}$	5.3	-	84
$\text{H}_2\text{Trien}^{2+}$	0.097	-	84
$\text{H}_2\text{Tet}^{2+}$	0.32	-	84
H Dien <sup>+</sup>	6.2	-	84
H Trien <sup>+</sup>	9.3	-	84
H Tet <sup>+</sup>	13.3	-	84
H Pent <sup>+</sup>	16.0	-	84
glycinate	15.0	0.9	70
Diglycinate	21.0	1.2	70
Triglycinate	8.0	0.46	85
2-Aminomethylpyridine	32.0	-	86
Picolinic Acid			
(-O-NH <sup>+</sup> )	4.2	-	87
(-O-N)	36.0	-	87
Fusaric Acid			
(-O-NH <sup>+</sup> )	8.1	-	87
(-O-N)	39.0	-	87
Cysteine	110.0	-	88

...contd..

Table I.4(contd.)

Tyrosine	5.4	-	88
	14.0	-	89
Penicillamine	110.0	-	88
NTA	2000	-	90
EDTA	6000	-	91
HP <sub>2</sub> O <sub>7</sub> <sup>3-</sup>	2100	1.2	92
ATP <sup>4-</sup>	4000	1.0	93
HP <sub>3</sub> O <sub>10</sub>	6800	1.2	92
N-methylimidazole, MeHL	0.23	-	94
N-methylimidazole, MeL	4.5	-	94
3-methylhistidine, MeHL	2.1	-	94
O-phthalate	630	-	95
en	350	-	96
enH <sup>+</sup>	0.18	-	96
NN-dimeen	32.0	-	97
NN-dimeenH <sup>+</sup>	0.069	-	97
NN'-dimeen	43.0	-	97
NN'-dimeenH <sup>+</sup>	0.029	-	97
trimeen	2.9	-	97
trimeenH <sup>+</sup>	.0096	-	97
anthracilate	2.3	-	98
salicylate	5.3	-	98
5-sulphosalicyate	4.7	-	98
lactate	26.0	-	99
glycollate	2.2	-	100
tmen	0.48	-	104

On the basis of Eigen mechanism the rate-determining step of the formation reaction, involving loss of a solvent molecule, is effected slightly by the incoming ligand so that the value of  $k_o$  in a given solvent is expected to be roughly independent of the entering group. The large range of values of  $k_f$  found with different ligands (Table I.4) arises mainly from the  $K_{os}$  term. The value of  $K_{os}$  can be calculated using equation (15) <sup>101-104</sup>.

$$K_{os} = \frac{4\pi N_A a^3}{3000} \cdot e^{-U(a)/kT} \quad \dots (15)$$

$$\text{where } U(a) = \frac{Z_A Z_B e^2}{D} \left( \frac{1}{a} - \frac{\kappa}{1 + \kappa a} \right) \quad \dots (16)$$

$$\text{and } \kappa = \left( \frac{8\pi N_A e^2 I}{1000 DkT} \right)^{1/2} \quad \dots (17)$$

In these equations  $N_A$  is Avogadro number, 'a' is the distance of closest approach between two ions (in centimeters), 'k' is Boltzmann's constant (in ergs), 'T' is the absolute temperature, 'e' is the charge of an electron (in electrostatic units), 'D' is the bulk dielectric constant, 'I' is the ionic strength and  $Z_A$  and  $Z_B$  are the charges on ions A and B respectively. Introduction of  $K_{os}$  in Eq. (11) or (13) makes it possible to evaluate  $k_o$ , which is roughly independent of the incoming ligand.



### I.3.3 Dissociation Reaction of Nickel(II) Chelates :

Chelate dissociation reactions are much slower than their formation reactions. Mechanism given in equation (12) can also account for the dissociation rates of complexes bearing mono or bidentate ligands. According to this mechanism, the rate constant for the dissociation of complexes will be

$$k_d = k_{-o} \quad \dots\dots \text{(for monodentate)}$$

and

$$k_d = \frac{k_{ro} k_{-o}}{k_{-o} + k_{rc}} \quad \dots\dots \text{(for bidentate)}$$

when  $k_{-o} \gg k_{rc}$ ,  $k_d = k_{ro}$  i.e., dissociation rate constant depends on the opening of chelate ring, and if  $k_{-o} \ll k_{rc}$  then  $k_d = k_{ro} \cdot k_{-o}/k_{rc}$  i.e. dissociation rate constant depends on the rupture of second metal-ligand bond. Both these situations have been detected several times with bidentate and also multidentate leaving groups<sup>69,84,105-109</sup>. It has been found that acid accelerates the dissociation by several orders of magnitude<sup>15,110-112</sup>. After one donor atom is replaced by a solvent molecule, the acid assists the dissociation of a polydentate chelate complex by protonating the partially coordinated intermediate and stabilizing it relative to the fully coordinated form. Some data of dissociation rate constants of octahedral nickel(II) chelates are given in Table I.5.

Table I.5. Kinetic data for dissociation of nickel chelates at 25°C in acidic media.

System	log $k_d$	Ref.	System	log $k_d$	Ref.
Ni(en) <sub>3</sub> <sup>2+</sup>	1.95	109	Ni(Phen) <sub>3</sub> <sup>2+</sup>	5.11	113,114
	1.85	110	Ni(Phen) <sub>2</sub> <sup>2+</sup>	-4.74	113,114
Ni(en) <sub>2</sub> <sup>2+</sup>	0.75	104	Ni(Phen) <sup>2+</sup>	-5.0	113,115
Ni(en) <sup>2+</sup>	-0.84	104	Ni(trien) <sup>2+</sup>	-4.75	84
	-0.97	110	Ni(NH <sub>3</sub> ) <sup>2+</sup>	0.76	110
Ni(bn) <sub>2</sub> <sup>2+</sup>	-0.59	104	Ni(tetra-meen) <sub>2</sub> <sup>2+</sup>	1.25	116
Ni(bn) <sup>2+</sup>	-1.69	104	Ni(GEDTA) <sup>2-</sup>	-2.60	117
			Ni(isoquinoline)	1.47	118
Ni(gly) <sub>3</sub> <sup>-</sup>	2.36	104	Ni(SCN) <sup>+</sup>	1.01	118
Ni(gly) <sub>2</sub>	1.32	109	Ni(α NPN )	2.21	119,120
Ni(gly) <sup>+</sup>	-0.27	109	Ni(α NPN-6-SO <sub>3</sub> )	2.11	119,120
Ni(TG) <sup>-</sup>	4.97	111	Ni(α NPN-3-6 diSO <sub>3</sub> )	1.69	119,120

Attempts at finding correlation between the kinetic effects of either the leaving group or the other bonded ligands and extra kinetic parameters have some times been successful. It has been shown<sup>121-123</sup> that the basicity of a leaving group is very important in determining the rate of dissociation of metal chelates. For example, rate of dissociation of  $\text{Ni}(x\text{-Py})(\text{H}_2\text{O})_5^{2+}$ , (where  $x = 3$  and 4-CN, Me, Br, OMe, 3-CONH<sub>2</sub> and 3-NH<sub>2</sub>) in acid solution increases linearly with decrease in the basicity of the leaving amine<sup>121</sup>;  $\log k_d = (1.5 - 0.21\text{p}K_a)$ . Also while the rate of dissociation is affected by  $\sigma$  donor ligand, it remains unaffected in the presence of  $\sigma$  donor  $\pi$  acceptor ligands<sup>50,124,125</sup>.

Some useful background kinetic information is provided by a polarographic study of the dissociation of the some chelates of nickel(II) with amino carboxylates viz. EDMA, HEDTA<sup>126</sup> and GEDTA<sup>117</sup>. The dissociation of  $\text{Ni}(\text{GEDTA})^{2-}$  and other amino-carboxylate complexes of nickel(II) is through a glycinate or an ethylenediamine chelate ring intermediate<sup>117,126-129</sup>.

#### I.3.4 Ligand Displacement Reactions :

Generally there are four types of exchange reactions that can take place:

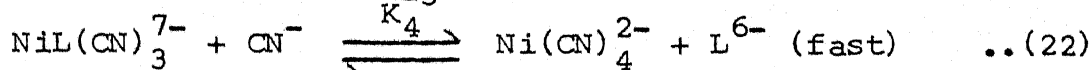
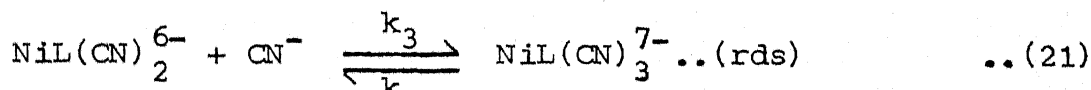
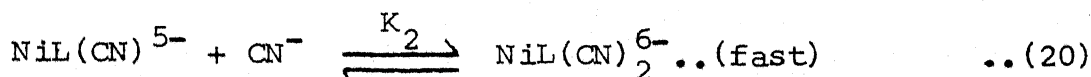
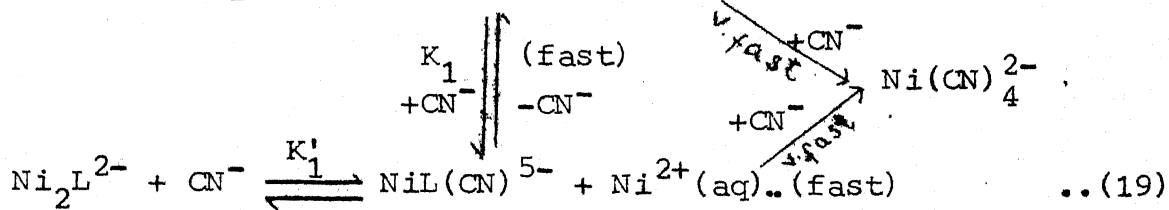
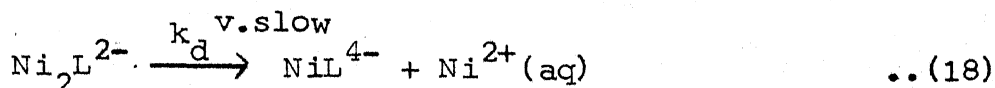
1. Monodentate ligand exchange reactions (excess ligand).
2. Multidentate ligand exchange reactions (excess ligand).
3. Metal exchange between ligands (excess metal)
4. Double exchange reactions.

The above exchange reactions are often slow because they involve the breaking of a series of coordinated bonds in succession.

#### I.3.4a Monodentate Ligand Exchange Reactions:

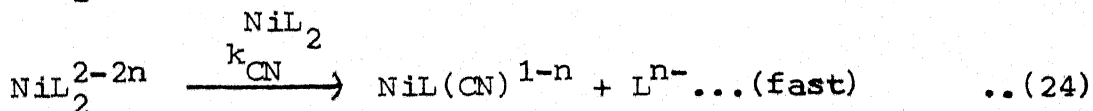
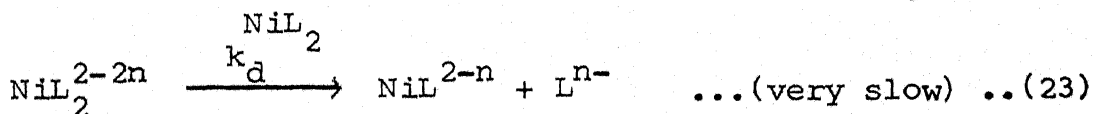
The kinetics and mechanism of exchange reactions of unidentate and multidentate ligands by unidentate ligands have been investigated in some detail<sup>41-46,130-144</sup>. Some data is also available on the exchange reaction of cyanide ion with some nickel(II) complexes of macrocyclic quadridentate N-donor ligands<sup>145-149</sup>. Cyanide ion is capable of displacing aminocarboxylates from their nickel(II) complexes<sup>41-43,133-142</sup>. The general mechanism for this class of replacement reactions requires that three cyanides are bonded to nickel(II) in the rate-determining step. A multistep mechanism via formation of mixed ligand intermediates is proposed for all these reactions.

Very little is known about the reactions of cyanide ion with binuclear complexes of nickel(II). Recently Nigam et al.<sup>150</sup> have reinvestigated the reaction of cyanide with a binuclear complex  $\text{Ni}_2\text{TTHA}$  studied earlier by Stara and Kopanica<sup>138</sup>. Nigam et al.<sup>150-152</sup> have proposed a different mechanistic scheme in which  $\text{Ni}_2\text{L}$  dissociates very slowly into  $\text{NiL}$  and  $\text{Ni}^{2+}_{(\text{aq})}$  which react further with excess  $\text{CN}^-$  present in the system to form  $\text{Ni}(\text{CN})_4^{2-}$ . The whole mechanistic scheme is outlined below:



The important step in the scheme is the cyanide assisted dissociation of  $\text{Ni}_2\text{L}$  to give  $\text{NiL}(\text{CN})$  and  $\text{Ni}^{2+}(\text{aq})$  both of which react with cyanide to finally form  $\text{Ni}(\text{CN})_4^{2-}$ .

On the other hand some bis complexes of aminocarboxylates react with cyanide ion according to following scheme,<sup>135,153</sup> followed by the rapid conversion of  $\text{NiL}(\text{CN})$  to  $\text{Ni}(\text{CN})_4^{2-}$ .



Billo<sup>142</sup> and Pearson et al.<sup>143</sup> have investigated the reaction of cyanide ion and square planer complexes of nickel(II) with 1,5 diazacyclooctane (dacco) and dithiooxalate (dto) respectively. Both reactions proceed through formation of

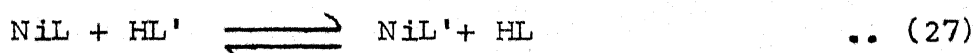
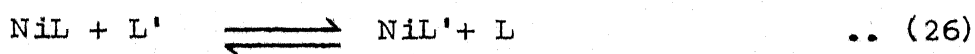
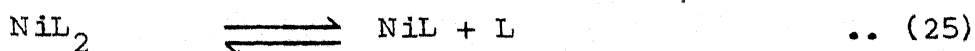
very stable mixed ligand complexes. This type of mixed ligand complexes were detected in some previous studies also e.g. in the reaction of dithioxalate<sup>142</sup> and 1,10 phen<sup>144,153</sup> complexes of nickel(II) with cyanide. The reaction of cyanide ion with the cation  $\text{Fe}(\text{L-L})_3^{2+}$ , where L-L is 1,10 phen<sup>155</sup> or a substituted phen<sup>156,157</sup>, Schiff's base<sup>158</sup>, bipy<sup>159-163</sup>, substituted bipy<sup>164</sup> or terpy<sup>165,166</sup> proceed in the same way initially forming mixed ligand complexes of type  $\text{Fe}(\text{L-L})_2(\text{CN})_2$ .

#### I.3.4b Multidentate Ligand Exchange Reactions:

The mechanism by which one multidentate ligand displaces another from a metal ion depends on the ability of both ligands to coordinate with the metal ion simultaneously. The rate-determining step of the overall reaction is the cleavage of any one of the several bonds between nickel(II) and the leaving group which must be broken in the course of reaction. For instance,  $\text{Ni}(\text{trien})^{2+}$  reacts with EDTA<sup>167</sup> or HEEDTA<sup>168</sup> rapidly giving a mixed-ligand complex,  $\text{Ni}(\text{Trien})\text{L}$ , where L is EDTA or HEEDTA. This undergoes successive unwrapping of Trien and increasing coordination of  $\text{L}^{n-}$  finally yielding  $\text{NiL}^{2-n}$ . On the other hand, formation of mixed-ligand intermediate complexes in the chelate substitution reaction of  $\text{Ni}(\text{EDDA})$  and  $\text{Ni}(\text{NTA})$  with Par is a relatively slow process<sup>40</sup>. Mixed ligand complexes have been experimentally recognised or kinetically inferred as reaction intermediates in several other cases of chelate substitution reactions<sup>132-135,167-172</sup>.

Octahedral complexes of nickel(II) in which the ligands occupy all the six coordination sites usually undergo substitution through the cleavage of one or more metal-ligand bonds before the incoming ligand enters the coordination sphere.

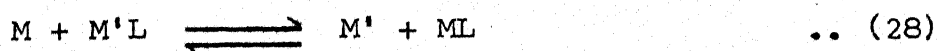
Bis complexes of nickel,  $\text{NiL}_2$ , generally involve release of the ligand L with a multidentate aminocarboxylate as an entering ligand<sup>126-129,173-177</sup>. In these cases the reaction rates are found to be strongly effected by acidity of the medium according to a rate law which is satisfactorily accounted for the following reaction scheme.



The reaction steps given in Eqns. (25,26) are also found to follow for ligand substitution reactions of several 1:1 complexes<sup>173,177-182</sup> of nickel(II).

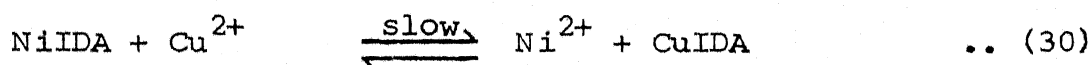
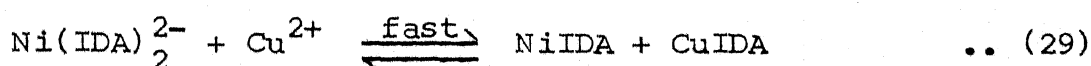
#### I.3.4c Metal Exchange Between Ligands :

Multidentate ligand transfer between two metal ions, as represented by Eqn. (28) has been extensively studied for a variety of metal ion combinations and aminocarboxylate ligands under widely different conditions<sup>23,37,38,183-192</sup>.



It has been supposed that a binuclear intermediate exists in such type of reactions and that the stability of these intermediates greatly influences the rates<sup>193,194</sup>.

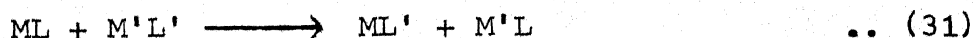
Recently Steinhaus et al.<sup>184</sup> have reported the metal exchange reaction of bis(iminodiacetato) nickelate(II) and copper(II) following a consecutive step type of mechanism (Eqns. 29,30).



The evidence for stepwise unwrapping mechanism followed by copper attack to give a dinuclear intermediate has been discussed for both steps by these authors at length.

#### I.3.4d Double Exchange Reactions :

Olson and Margerum<sup>195</sup> have reported an interesting example of a coordination chain reaction involving exchange between two complexes



The reaction is initiated by the dissociation of a very small quantity of one of the complexes or by the addition of traces of free ligand L or L'. The two free multidentate





$L(H_2O)_{n-1}NiL-L$ , the observed rate constants for the formation and dissociation of  $(H_2O)_{n-2}LNi \begin{smallmatrix} L \\ \diagup \diagdown \\ L \end{smallmatrix}$  are given respectively by.

$$k_f = \frac{K_{os} k_{12} k_{23}}{k_{21} + k_{23}} \quad \dots (35)$$

and

$$k_d = \frac{k_{21} k_{32}}{k_{21} + k_{23}} \quad \dots (36)$$

The effect of already-bound ligands on the ease of water replacement during the formation of ternary complexes can be summed up in the following statements<sup>202</sup>:

(i) A reduction in  $k_f$  is expected on statistical grounds since the number of replaceable water molecules is reduced. This can be allowed for by multiplying the measured  $k_f$  by an appropriate statistical factor to give  $k_f$ . (ii) Strengthening of the metal-ligand bonds could be accompanied by a weakening of the remaining metal-water bond. This would result in an increase in  $k_f$  and a decrease in  $\Delta H_f^\ddagger$ . (iii) The value of  $k_{32}$  could be reduced, thus allowing ring closure to contribute to the rate-determining step. (iv) In the case of a negatively charged incoming ligand  $L-L$ ,  $K_{os}$  would be reduced if  $L$  was also charged since the net positive charge on the metal ion would be reduced. Some kinetic data for the formation of ternary complexes are given in Table I.6.

Table I.6. Kinetic data for the formation of ternary complexes of nickel(II) in water at 25°C.

Complex	Ligand(Ref.)		
	NH <sub>3</sub> (124)	nsa (202)	Pada (201)
	$k_{f,m}^{s,m^{-1}s^{-1}}$	$k_{f,m}^{s,m^{-1}s^{-1}}$	$k_{f,m}^{s,m^{-1}s^{-1}}$
NiEDDA	-	$2.6 \times 10^4$	-
NiIDA	$5.3 \times 10^3$	$6.3 \times 10^5$	$1.3 \times 10^4$
NiNTA <sup>-</sup>	$1.4 \times 10^4$	$1.5 \times 10^4$	$1.3 \times 10^4$
Nidien <sup>2+</sup>	$7.8 \times 10^4$	$1.5 \times 10^6$	$9.4 \times 10^4$
NiTrien <sup>2+</sup>	$1.0 \times 10^{6a}$	$4.6 \times 10^6$	$7.5 \times 10^4$
NiTren <sup>2+</sup>	$2.0 \times 10^{6b}$	$5.2 \times 10^6$	$5.5 \times 10^4$
NiTP <sup>3-</sup>	-	$1.48 \times 10^4$	$4.0 \times 10^3$

a Estimates based on the value quoted at 8°C<sup>205</sup>.

b Estimates based on the value quoted at 6°C<sup>205</sup>.

s Stands for solvent.

Melvin et al.<sup>206</sup> have reported the rate of formation of phen, bipy, and terpy complexes of  $\text{Ni(en)}^{2+}$ ,  $\text{Ni(dien)}^{2+}$  and  $\text{Ni(en)}_2^{2+}$  in aqueous solution and found that the rate increases as the number of coordinated nitrogens increases. This may be due to the increase in water exchange rate in the presence of bound ligand, which is found to increase as the number of coordinated nitrogens increases<sup>207</sup>. Cayley and Margerum<sup>208</sup> attributed the increase in rate of ternary complex formation to the stacking interaction of incoming ligands with already coordinated ligands. Stacking interactions are important in many areas of chemistry ranging from the stability of ternary transition metal complexes<sup>209-213</sup> to the structure of DNA<sup>214</sup>. Stacking interactions will assist the substitution process only if the incoming ligand is sufficiently flexible to permit one donor group to become oriented in a position suitable for replacing a coordinated water molecule while the rest of the molecule is in a stacked arrangement. Larger the area of interaction between the stacking molecules greater is the formation rate constant. The volume of activation for the reaction of Pada with five substituted nickel(II) species have been recorded<sup>215</sup>. They fall into two group,  $+3 \text{ cm}^3 \text{ mol}^{-1}$  (when the bound ligand is tren or trien) and  $+6 \text{ cm}^3 \text{ mol}^{-1}$  (where the ligand is nta<sup>3-</sup>, edda<sup>2-</sup> or dien). The latter value is interpreted in terms of the normal  $I_d$  mechanism in which the water-replacement step is rate-determining, while the former is interpreted in terms of a mechanism in which ring closure is rate-limiting.

### I.3.6 Solvent effect in Ligand Substitution Reactions :

Interest in the effect of solvents and salts on the reactivity in inorganic systems appears to be growing in the past few years. Some relevant reviews include a general discussion on the solvent effect both for inorganic and organic reactions in mixed aqueous media<sup>216-218</sup>. A yet another review appeared on the solvent effects in reactions of square planer complexes only<sup>219</sup>. The effect of solvent on the rate may be primarily due to (a) change in the dielectric constant of media, (b) change in the viscosity, (c) change in solvent polarity and (d) water concentration.

Caldin and Bennetto have developed a very interesting mechanistic picture which seeks to take solvent effects explicitly into account<sup>220,221</sup>. This picture is applied to reactions in non-aqueous solvents as well as water. A critical appraisal of the caldin-Bennetto view point has been given by Chattopadhyay and Coetzee while concluding their views on the substitution reactions of nickel(II) ion with pyridine, 2,2'-bipy, 1,10 Phen and 2,2',2''-terpy, mainly in acetonitrile and dimethyl sulfoxide (DMSO) as solvents. In DMSO, substitution by pyridine appears to proceed by an  $I_d$  mechanism, but with multidentate ligands at ordinary temperature the possibility exists that the rate controlling steps is ring closure. Unlike most monodentate ligands whose behaviour is comparable to that in aqueous solution, certain polydentate ligands either react very fast or slow

compared to unidentate ligands in the same solvent. The reaction of bipy<sup>221-224</sup> with nickel in methanol is 25 times slower while that of 5,6 dimethylphenanthroline<sup>223</sup> in acetonitrile is 70 times faster at 25°C compared to the rate in aqueous solution<sup>222,226-228</sup>.

Variation in the formation and dissociation rate constants for nickel(II) malonate in water-dioxane mixture<sup>224</sup> is due to changes in the ion-pair formation constant, which is sensitive to the dielectric constant of the solvent as in the reaction of Ni(II) with a series of ligands in DMF<sup>118</sup>, acetonitrile<sup>230</sup> and methanol<sup>231-234</sup>.

Cusumano<sup>235</sup> has reported the complexation of nickel(II) in non-aqueous solvents with some azo-dyes and concluded that the process of complexation is governed by a sterically controlled mechanism.

In brief, the path ways for ligand substitution reactions between nickel(II) and mono, bi or tridentate ligands can be accommodated within the general framework of an  $I_d$ -type mechanism, if the effects of possible fine interactions between solvent and solute are considered. The stability of the outersphere complex and the orientation of ligand in the outer-sphere complex are important factors in  $I_d$ -type mechanism. Both factors are influenced by (i) the effective positive charge on the metal ion, which is determined by donor strength of the solvent, (ii) the

interaction distance between the ligand and metal ion which is governed by thickness of the inner sphere complex and

(iii) competition between the ligand and the solvent in the outer-sphere complex.



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## CHAPTER II

### KINETICS AND MECHANISM OF TETRACYANO NICKELATE(II) FORMATION FROM BINUCLEAR Ni(II) CHELATES: REACTION OF MONO (ETHYLENEDIOXY) DIETHYLENEDINITRILLO TETRA- ACETATO DINICKELATE(II) WITH CYANIDE IONS

#### ABSTRACT

The kinetics of ligand substitution reaction of binuclear nickel(II) chelate,  $Ni_2L$ , where L is EGTA ((ethylenedioxy) diethylenedinitrilo tetraacetic acid) with cyanide ion has been investigated spectrophotometrically. The reaction conditions are  $pH = 11.0 \pm 0.1$ ,  $I = 0.1M$  ( $NaClO_4$ ) and  $temp. = 25 \pm 0.1^\circ C$ . The formation of  $Ni(CN)_4^{2-}$  is first order in  $Ni_2L$  and first order in cyanide in a large range of cyanide concentration. However, at low cyanide concentration i.e., below  $10^{-3}M$ , the reaction becomes zero order in cyanide. These results indicate the presence of a slow dissociation step in which  $Ni_2L$  dissociates to give  $NiL^{2-n}$  and  $Ni^{2+}_{(aq)}$  at low cyanide concentration and a cyanide assisted rapid dissociation of  $Ni_2L$  to produce  $NiL(CN)_2^{2-n-x}$  and  $Ni^{2+}_{(aq)}$  at higher cyanide concentration.

These species react with excess cyanide finally producing  $\text{Ni}(\text{CN})_4^{2-}$ . A five step mechanism has been proposed and the rate determining step has been identified.

The forward rate expression has the form

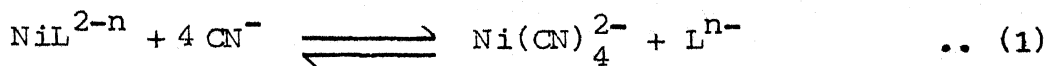
$$\text{rate} = (k_d + k') [\text{Ni}_2\text{L}] = k_{\text{obsd}} [\text{Ni}_2\text{L}]$$

where  $k_d$  ( $= (3.9 \pm 0.4) \times 10^{-3} \text{ sec}^{-1}$ ) is the cyanide independent dissociation rate constant of  $\text{Ni}_2\text{L}$  and  $k' = k_f [\text{CN}^-]^{3-x}$  where  $x = 2$  consistent with first order dependence in cyanide in this case. The term  $k_f$  is made up of rate constants and equilibrium constants. The value of  $k_f$  in this case is  $8.1 \pm 0.5 \text{ M}^{-1}\text{s}^{-1}$ . The backward reaction rate was first order in  $\text{Ni}(\text{CN})_4^{2-}$  and EGTA each, and inverse first order in free cyanide. The backward rate constant  $k_r$  (i.e.  $K_4^{-1}k_{-3}$ ) is  $(7.1 \pm 0.5) \times 10^{-8} \text{ s}^{-1}$  at  $I = 0.3\text{M}$ . From an analysis of the  $[\text{H}^+]$  dependence of forward reaction rate over a pH range of 7.5-11.0, it is inferred that between pH 7.5-9.0, one molecule of HCN is involved in the reaction besides two cyanide ions. The activation parameters for forward and backward reactions have also been evaluated.

## II.1 INTRODUCTION

A considerable amount of data is now available on the formation of tetracyanonickelate(II) from mononuclear nickel(II) complexes of aminocarboxylates<sup>1-10</sup>, polyamines<sup>11,12</sup> as well as

aquonickel(II)<sup>13-15</sup>. Cyanide ions react with mono(aminocarboxylato) complexes of nickel(II) to form  $\text{Ni}(\text{CN})_4^{2-}$  complex releasing the aminocarboxylate ligand according to equation



But the kinetic and mechanistic studies on the binuclear complexes of nickel(II) have attracted little attention so far<sup>16-18</sup>. We had occasion to reinvestigate the reaction between  $\text{Ni}_2\text{TTHA}$  and cyanide, earlier reported by Stara and Kopanica<sup>16</sup>, and to disprove their mechanism<sup>17,18</sup>. We also undertook the study of  $\text{Ni}_2\text{DTPA-CN}^-$  reaction to gain further understanding of the reaction pathways of binuclear complexes in substitution processes.

In this work the kinetics and mechanism of the substitution reaction of another binuclear complex of Ni(II) viz.  $\text{Ni}_2\text{EGTA}$  with cyanide ion has been investigated and interpreted in further support of the mechanism proposed by us<sup>18</sup>.

## II.2 Experimental Section

EGTA was obtained through the courtesy of Geigy Chemical Co. (Switzerland) and was recrystallised twice by dissolving the acid in hot water with the aid of sodium hydroxide and precipitating the same by adjusting the pH of the solution to 2 with dilute  $\text{HClO}_4$ . The recrystallised acid was dried in an oven at  $110^\circ\text{C}$ . It was standardised by potentiometric titration against carbondioxide free NaOH solution. Nickel perchlorate, supplied



by Alpha Inorganics, was recrystallised before use. A stock solution of  $\text{Ni}(\text{ClO}_4)_2$  was standardised against EDTA by complexometric titration<sup>19</sup>. A solution of  $\text{Ni}_2\text{EGTA}$  was prepared by adding a slight excess of nickel ion over stoichiometric amount of EGTA and removing excess nickel as  $\text{Ni}(\text{OH})_2$  at pH 10 by millipore filtration using 0.45  $\mu\text{m}$  filter. The clear solution of  $\text{Ni}_2\text{EGTA}$  was standardised by the addition of a fifty fold excess of  $\text{NaCN}$  at pH 11.0. After allowing for complete conversion to  $\text{Ni}(\text{CN})_4^{2-}$  the absorbance was measured at 267 nm ( $\epsilon_{\text{Ni}(\text{CN})_4^{2-}} = 1.16 \times 10^4$ ) using suitable dilution.

All other chemicals were of AR grade and were used without further purification. All solutions were prepared in double distilled water. All pH measurements were made on an Elico Digital pH meter model LI-120. A Toshniwal Spectrophotometer model RL-02 was used for the study of slow reactions. A SF-3A stopped Flow Spectrophotometer from Hitech (England) coupled to a storage oscilloscope model OS-768S of ECIL (India) was used for the study of fast reactions.

### II.3 KINETIC RUNS

From the electronic spectra of  $\text{Ni}_2\text{EGTA}$  (Fig. II.1) one can see that  $\text{Ni}_2\text{EGTA}$  complex absorbs in the visible region and has two absorption peaks at 380 and 625 nm. But the reaction product viz.  $\text{Ni}(\text{CN})_4^{2-}$  gives 2 sharp peaks at 267 and 285 nm. (Fig. II.2). The reaction was monitored either at 267 or 285 nm by following

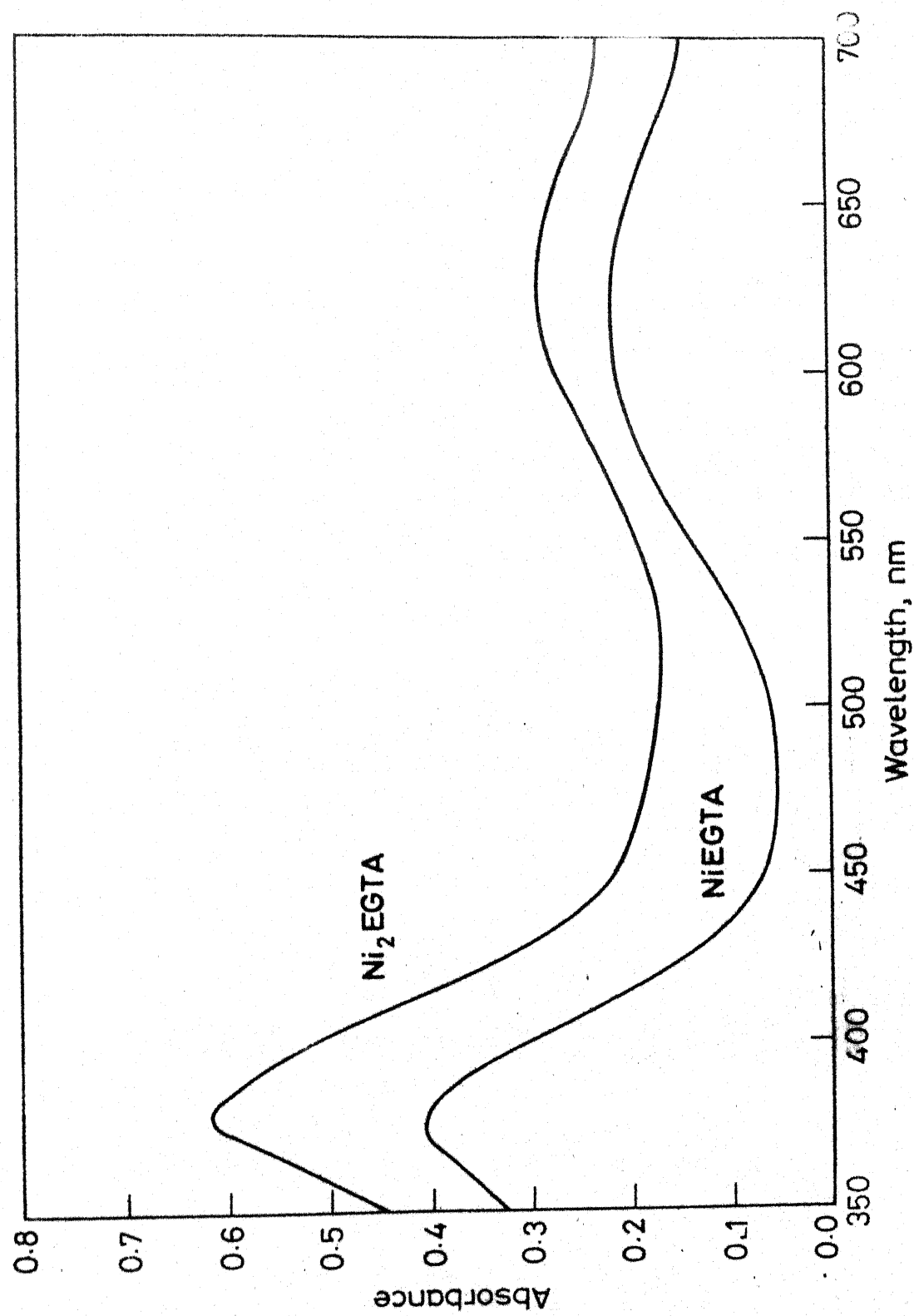


Fig. II.1 Absorption spectra of  $\text{NiEGTA}$  and  $\text{Ni}_2\text{EGTA}$  complexes;  $[\text{NiEGTA}] = 5.0 \times 10^{-2} \text{ M}$ ,  $[\text{Ni}_2\text{EGTA}] = 2.0 \times 10^{-2} \text{ M}$ .

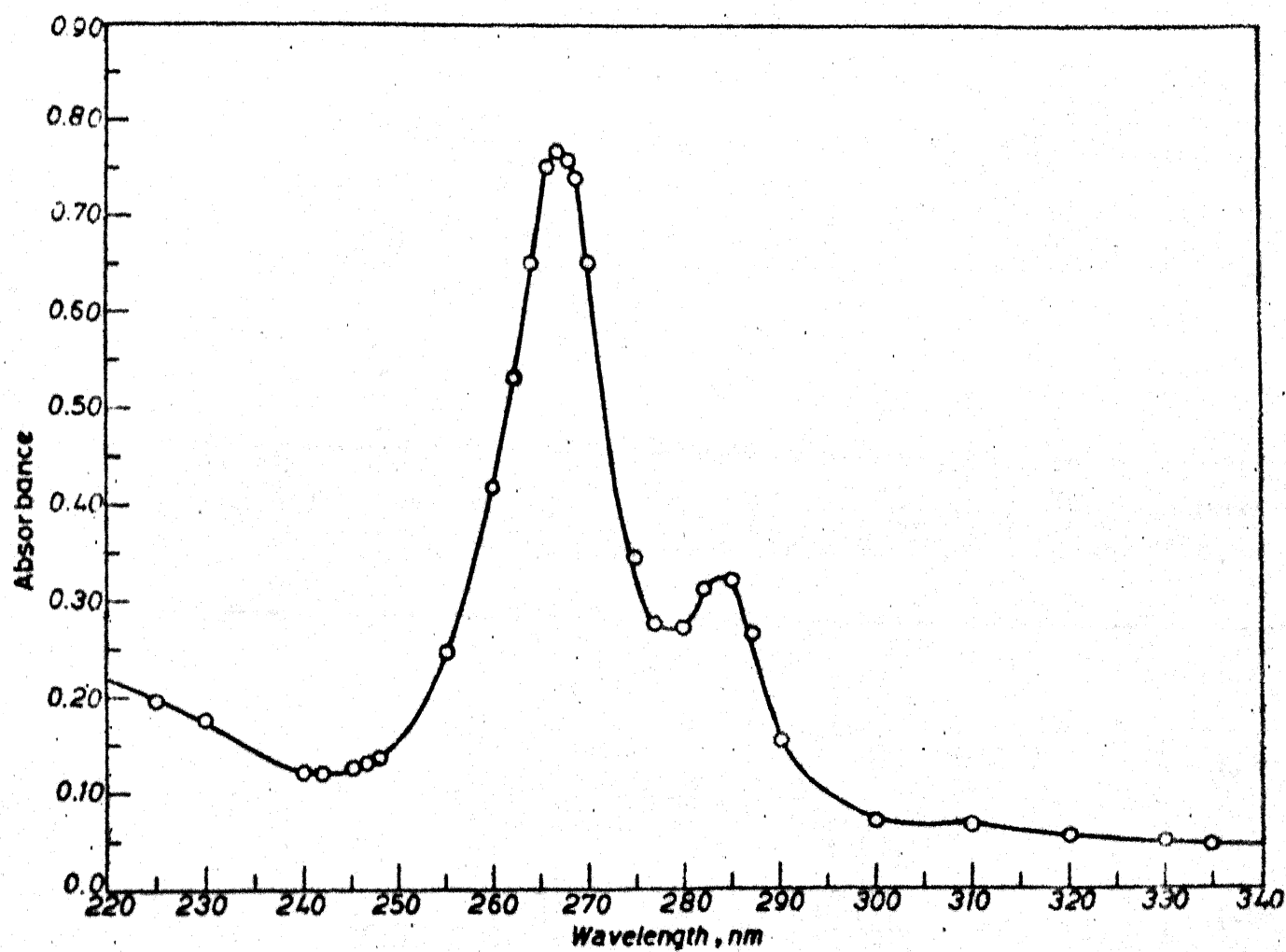


Fig II.2 Absorption spectra of  $\text{Ni(CN)}_4^{2-}$ ;  $[\text{Ni(CN)}_4^{2-}] = 7.0 \times 10^{-5} \text{ M}$ .

the concentration of  $\text{Ni}(\text{CN})_4^{2-}$  as a function of time. At these wavelengths  $\text{Ni}_2\text{L}$  and cyanide ion do not absorb appreciably.

## II.4 RESULTS

### II.4.1 Kinetics of forward reaction of $\text{Ni}_2\text{L}$ with cyanide ion:

Potentiometric titration data indicate that EGTA forms a mononuclear as well as a binuclear complex with nickel(II)<sup>20</sup>. A computer calculation using the overall stability constant value for  $\text{Ni}_2\text{EGTA}$  and the protonation constant values of EGTA (Table II.1) shows that starting with a metal to ligand ratio of 2:1 the

Table II.1. Protonation and Equilibrium Constants (log values) of EGTA and its nickel complexes<sup>20</sup> at 20°C and I=0.1M

$K_{\text{HL}}$	9.46	$K_{\text{NiL}}$	13.6
$K_{\text{H}_2\text{L}}$	8.85	$K_{\text{NiHL}}$	8.3
$K_{\text{H}_3\text{L}}$	2.65	$K_{\text{NiL}}$ $K_{\text{NiHL}}$	6.0
$K_{\text{H}_4\text{L}}$	2.00	$K_{\text{NiL}}$ $K_{\text{Ni}_2\text{L}}$	4.9

binuclear complex viz.  $\text{Ni}_2\text{EGTA}$  is the predominant chemical species (80-85%) between pH 7.5-11.0. The forward reactions were run at temp. = 25°C, pH = 11.0 ± 0.1 and I = 0.1M ( $\text{NaClO}_4$ ) in the presence of excess cyanide under pseudo first order conditions.

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The rate constants were evaluated from plots of  $\log (A_{\infty} - A_t)$  versus  $t$ . They were found to be first order in  $Ni_2L$  and first order in cyanide over a wide concentration range. The observed pseudo first order rate constants are given in Table II.2 along with their standard deviations (at least 4 to 6 runs) and are also plotted as  $\log (k_{obsd})$  versus  $\log [CN^-]_T$  in Fig. II.3,  $[CN^-]_T$  includes cyanide present in all its forms:

Table II.2. Rate constants for the Reaction of  $Ni_2EGTA$  complex with cyanide at  $25^{\circ}C$ ,  $pH = 11.0$  and  $I = 0.1M$  ( $NaClO_4$ ).

$[CN^-]_T, M$	$[Ni_2L], M$	$k_{obsd} \times 10^2 \text{ sec}^{-1}$
$2.00 \times 10^{-4}$	$1.15 \times 10^{-5}$	$0.31 \pm .06^a$
$2.75 \times 10^{-4}$	$1.15 \times 10^{-5}$	$0.34 \pm .04^a$
$4.0 \times 10^{-4}$	$1.15 \times 10^{-5}$	$0.40 \pm .02^a$
$6.4 \times 10^{-4}$	$1.2 \times 10^{-5}$	$0.37 \pm .04^a$
$8.0 \times 10^{-4}$	$1.2 \times 10^{-5}$	$0.40 \pm .03^a$
$2.0 \times 10^{-3}$	$2.3 \times 10^{-5}$	$1.52 \pm .09$
$3.0 \times 10^{-3}$	$2.3 \times 10^{-5}$	$2.70 \pm 0.1$
$4.0 \times 10^{-3}$	$2.4 \times 10^{-5}$	$3.12 \pm 0.2$
$9.44 \times 10^{-3}$	$2.4 \times 10^{-5}$	$6.70 \pm 0.4$
$1.11 \times 10^{-2}$	$2.4 \times 10^{-5}$	$8.25 \pm 0.7$
$2.22 \times 10^{-2}$	$2.5 \times 10^{-5}$	$20.3 \pm 0.6$
$4.27 \times 10^{-2}$	$2.5 \times 10^{-5}$	$39.8 \pm 1.0$

(a) zero order rate constants in cyanide

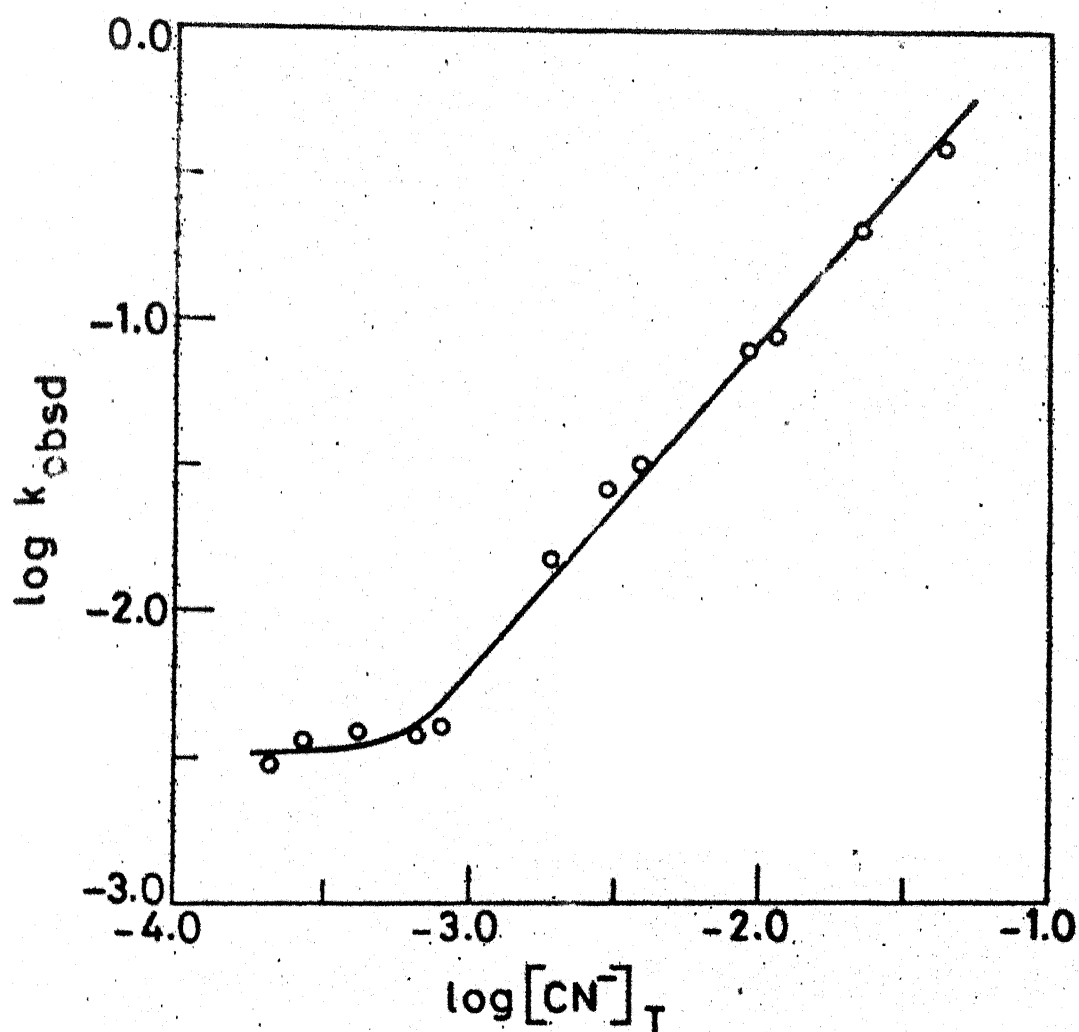
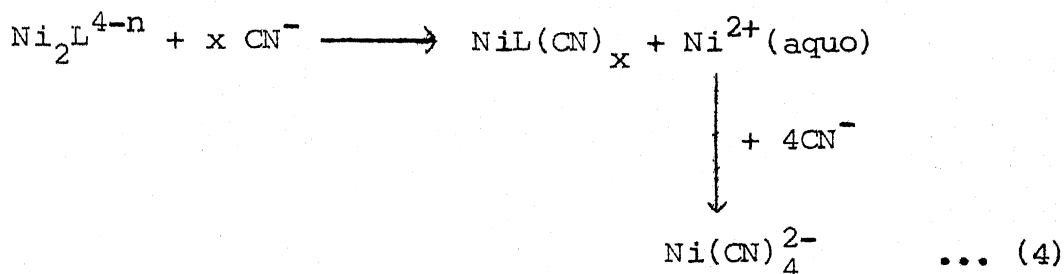


Fig. II.3 Cyanide dependence of the observed forward rate constants for the reaction of  $\text{Ni}_2\text{EGTA}$  with cyanide ion, temp. =  $25^\circ\text{C}$ ,  $\text{pH} = 11.0 \pm 0.1$  and  $I = 0.1\text{M}$ .



In the presence of cyanide, the  $\text{Ni}_2\text{L}$  complex gives  $\text{NiL}(\text{CN})_x$  and  $\text{Ni}^{2+}(\text{aq})$  and cyanide assists this dissociation. The species  $\text{NiL}$  (produced according to Eqn. 2),  $\text{NiL}(\text{CN})_x$  and  $\text{Ni}^{2+}(\text{aq})$  react further with excess cyanide finally forming  $\text{Ni}(\text{CN})_4^{2-}$ . The subsequent steps for reaction of the first two are same as far the reactions of mono aminocarboxylato nickel(II) complexes with cyanide<sup>1-4</sup>.

#### IL.4.2 Kinetics of Reaction between $\text{Ni}(\text{CN})_4^{2-}$ and EGTA:

This reaction, hence forth called the backward reaction, was found to proceed only in the presence of a large excess of ligand viz. EGTA. Only  $\text{NiL}$  is formed in this reaction and there is no evidence for the formation of  $\text{Ni}_2\text{L}$ . The rate of reaction depends upon the first power of concentrations of each,  $\text{Ni}(\text{CN})_4^{2-}$  and the ligand. It also showed an inverse first order dependence in free cyanide. The rate expression was formulated as

$$\frac{-d [\text{Ni}(\text{CN})_4^{2-}]}{dt} = \frac{k_r [\text{Ni}(\text{CN})_4^{2-}] [\text{L}^{n-}]}{[\text{CN}^-]} \qquad \dots (5)$$

The integrated form of this equation is

$$(A_i - A_t) + A_i \ln \frac{A_t}{A_i} = - \frac{\epsilon_1}{4} k'_{\text{obsd}} t \qquad \dots (6)$$

where  $A_i$  is the initial absorbance and  $A_t$  is the absorbance at time  $t$ ;  $\epsilon$  is the molar absorptivity of  $\text{Ni}(\text{CN})_4^{2-}$ ,  $l$  is the path length and  $k'_{\text{obsd}} = k_r [\text{L}^{n-}]$ . A plot of the left hand side of equation (6) vs time gives a straight line and slopes of these plots give  $k'_{\text{obsd}}$  and hence  $k_r$ . These values are given in Table II.3. A plot of  $k'_{\text{obsd}}$  vs  $[\text{EGTA}]$  is a straight line (Fig. II.4) with a slope equal to  $k_r$ . The value of  $k_r$  is found to be  $(7.1 \pm 0.5) \times 10^{-8} \text{ s}^{-1}$ .

Table II.3. Rate Constants for the Reaction of  $\text{Ni}(\text{CN})_4^{2-}$  with EGTA at  $25^\circ\text{C}$ ,  $I = 0.3\text{M}(\text{NaClO}_4)$ ,  $\text{pH} = 11.0 \pm 0.1$ ,  $[\text{Ni}(\text{CN})_4^{2-}] = 2.6 \times 10^{-5}\text{M}$ .

$[\text{EGTA}] \times 10^2, \text{M}$	$k'_{\text{obsd}} \times 10^{10}, \text{MS}^{-1}$	$k_r \times 10^8, \text{s}^{-1}$
0.25	$1.82 \pm 0.2$	$7.28 \pm 0.4$
0.50	$3.8 \pm 0.15$	$7.6 \pm 0.3$
1.00	$7.2 \pm 0.1$	$7.2 \pm 0.1$
1.20	$7.5 \pm 0.2$	$6.25 \pm 0.15$
		$\text{Av}(7.1 \pm 0.5) \times 10^{-8} \text{ s}^{-1}$

#### II.4.3 Temperature dependence

The temperature dependence of the rates of forward and backward reactions were investigated over a temperature range of



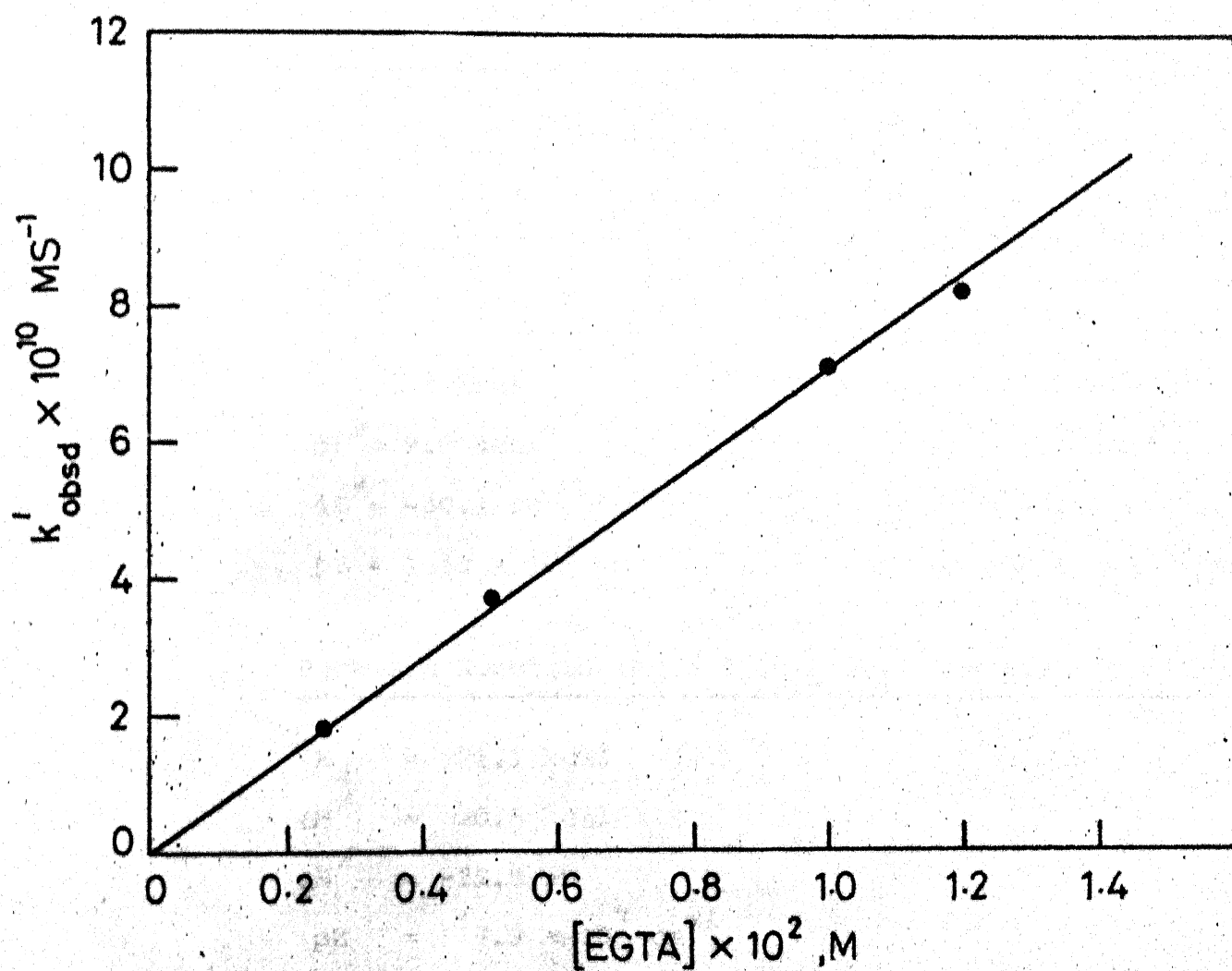


Fig. II.4 EGTA dependence of the observed rate constants for the reaction of  $\text{Ni}(\text{CN})_4^{2-}$  with EGTA. temp. = 25°C, pH = 11.0, I = 0.3M.

25-45°C and were found to obey the Arrhenius equation. The activation parameters for forward reaction have been evaluated for both the situations, i.e. where order dependence in cyanide is zero and one respectively. These data are given in Table II.4.

Table II.4. Activation Parameters for the forward and backward reactions per mole.

Forward Reaction (pH = 11.0  $\pm$  0.1, and I = 0.1M(NaClO<sub>4</sub>))

Zero order dependence	First order dependence
$E_a = 9.6$ kcal	$E_a = 6.1$ kcal
$\Delta H^\ddagger = 9.0$ kcal	$\Delta H^\ddagger = 5.5$ kcal
$\Delta S^\ddagger = -30.4$ eu	$\Delta S^\ddagger = -36.7$ eu
$pZ = 1.58 \times 10^6$ cm <sup>-1</sup>	$pZ = 8.5 \times 10^4$ cm <sup>-1</sup>

Backward Reaction (pH = 11.0  $\pm$  0.1, I = 0.3M (NaClO<sub>4</sub>))

$E_a = 21.1$ kcal
$\Delta H^\ddagger = 20.5$ kcal
$\Delta S^\ddagger = -22.5$ eu
$pZ = 7.9 \times 10^7$ cm <sup>-1</sup>

#### II.4.4 pH dependence of Ni<sub>2</sub>L-CN<sup>-</sup> Reaction

The pH dependence of the forward reaction is given in Fig. II.5, Table II.5. Under the conditions where order dependence

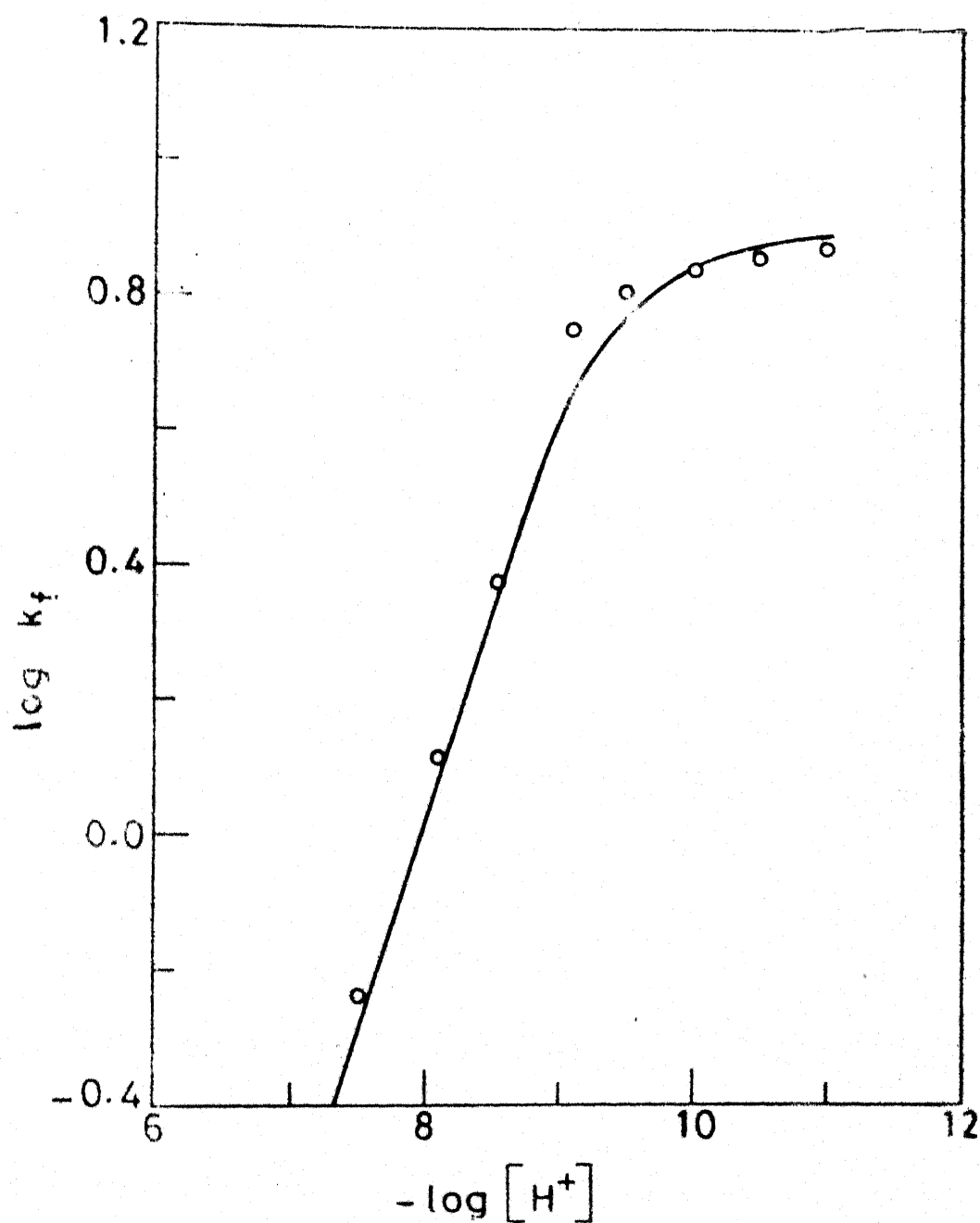


Fig. II-5 Effect of pH on the reaction of cyanide ion with  $Ni_2EGTA$ . Solid line is calculated from the resolved rate constants. (Conditions as given in Table II.5)

in cyanide is one. It was seen that the rate remains almost constant in the pH range 9.5-11; but it decreases below pH 9.0

Table II.5. Hydrogen ion dependence of the forward rate constant  
 $[\text{Ni}_2\text{EGTA}] = 2.58 \times 10^{-5} \text{M}$ ;  $[\text{CN}^-]_{\text{T}} = 2.0 \times 10^{-3} \text{M}$ ;  
 $\text{I} = 0.1 \text{M} (\text{NaClO}_4)$ ; temp. =  $25 \pm 0.1^\circ \text{C}$ .

$-\log [\text{H}^+]$	$k_{\text{obsd}}, \text{s}^{-1}$	$k_{\text{f}} = \frac{k_{\text{obsd}}}{[\text{CN}^-]_{\text{T}}}, \text{M}^{-1} \text{s}^{-1}$
7.5	$1.15 \times 10^{-3}$	0.57
8.1	$2.40 \times 10^{-3}$	1.20
8.5	$4.50 \times 10^{-3}$	2.25
9.1	$11.50 \times 10^{-3}$	5.75
9.5	$12.90 \times 10^{-3}$	6.45
10.0	$13.83 \times 10^{-3}$	6.92
10.5	$14.48 \times 10^{-3}$	7.24
10.7	$14.72 \times 10^{-3}$	7.36
10.9	$14.83 \times 10^{-3}$	7.41

as found also in our earlier studies<sup>1,8</sup> on  $\text{Ni}_2\text{TTHA}$  and  $\text{Ni}_2\text{DTPA}$  reactions. This is due to the formation of a less reactive species HCN below pH 9.0. The initial linear portion of the plot of  $\log k_{\text{f}}$  vs  $-\log [\text{H}^+]$ , ( $k_{\text{f}} = \frac{k_{\text{obsd}}}{[\text{CN}^-]_{\text{T}}}$ ) gives a slope equal to one (Fig. II.5). This value indicates that one HCN is involved in addition to two cyanides upto the rate determining

step below pH 9. A rate expression valid for the whole range of pH (7.5 to 11.0) is given below:

$$\frac{d [\text{Ni}(\text{CN})_4^{2-}]}{dt} = \{ k_{f(\text{CN})} [\text{CN}^-] + k_{f(\text{HCN})} [\text{HCN}] \} [\text{NiL}(\text{CN})_2] \quad \dots (7)$$

where  $k_{f(\text{CN})}$  and  $k_{f(\text{HCN})}$  are the rate constants for  $\text{CN}^-$  and  $\text{HCN}$  reactants respectively.

The resolution of the rate constants was done as follows:

$$k_f [\text{CN}^-]_T = k_{f(\text{CN})} [\text{CN}^-] + k_{f(\text{HCN})} [\text{HCN}] \quad \dots (8)$$

$$k_f \{ [\text{CN}^-] + [\text{HCN}] \} = k_{f(\text{CN})} [\text{CN}^-] + k_{f(\text{HCN})} K_{\text{HCN}} [\text{H}^+] [\text{CN}^-]$$

$$\text{or } k_f [\text{CN}^-] \{ 1 + K_{\text{HCN}} [\text{H}^+] \} = \{ k_{f(\text{CN})} + k_{f(\text{HCN})} K_{\text{HCN}} [\text{H}^+] \} [\text{CN}^-]$$

$$\text{or } k_f = \frac{k_{f(\text{CN})} + k_{f(\text{HCN})} K_{\text{HCN}} [\text{H}^+]}{1 + K_{\text{HCN}} [\text{H}^+]} \quad \dots (9)$$

where  $K_{\text{HCN}}$  is the protonation constant for  $\text{CN}^-$ . At pH below 9.0, one is negligible in comparison to  $K_{\text{HCN}} [\text{H}^+]$  and equation (9) reduces to equation (10)

$$k_f = \frac{k_{f(\text{CN})}}{K_{\text{HCN}}} \cdot \frac{1}{[\text{H}^+]} + k_{f(\text{HCN})} \quad \dots (10)$$

A plot of  $k_f$  vs  $\frac{1}{[\text{H}^+]}$  is a straight line (Fig. II.6). The slope of the straight line gives  $k_{f(\text{CN})} = 7.8 \text{ M}^{-1} \text{ s}^{-1}$  and the intercept gives  $k_{f(\text{HCN})} = 0.35 \text{ M}^{-1} \text{ s}^{-1}$ .

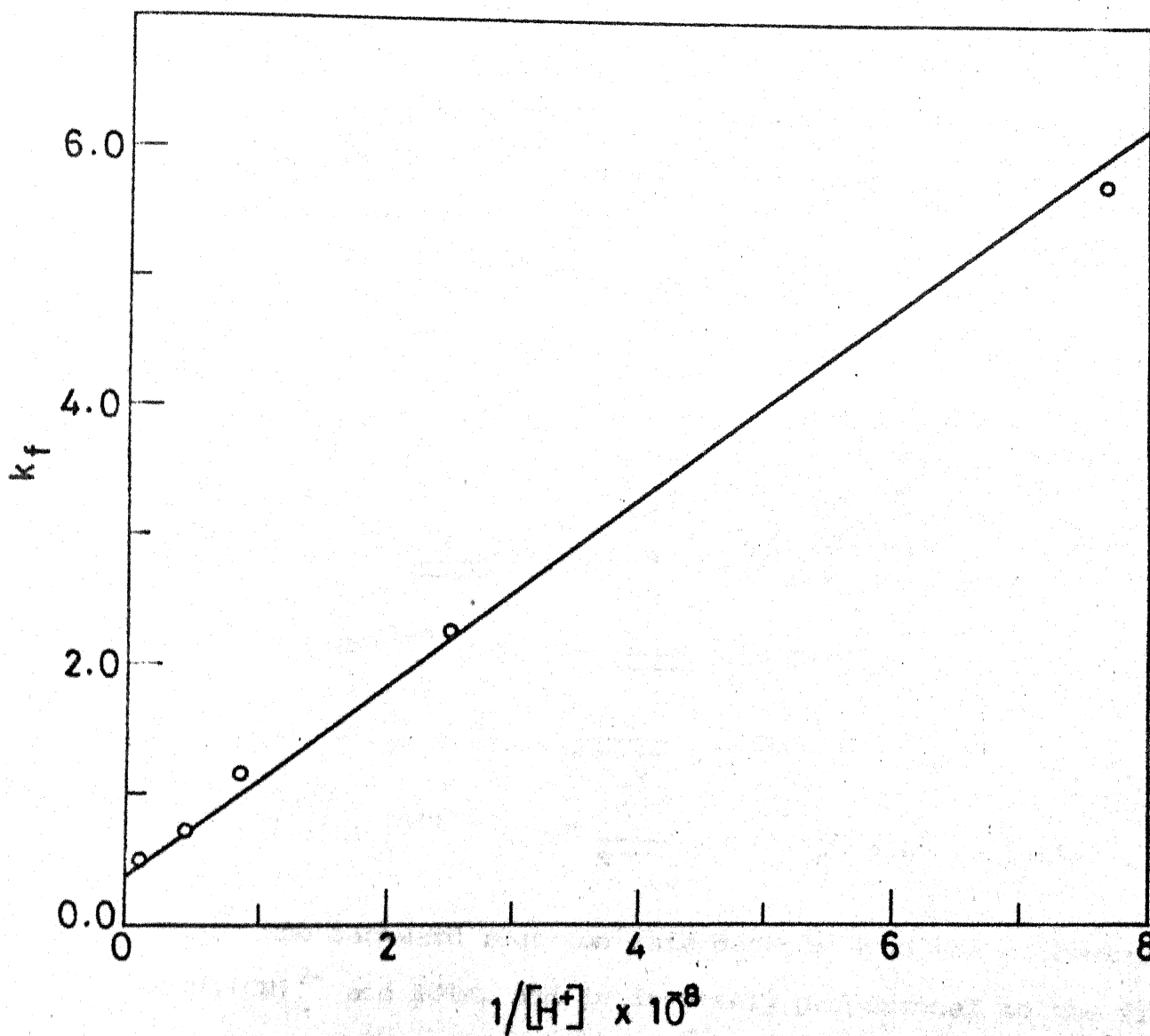
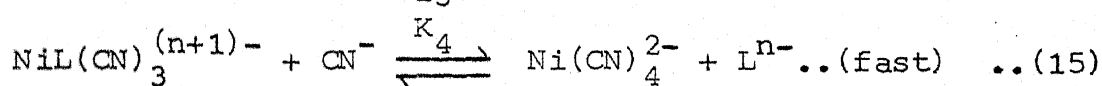
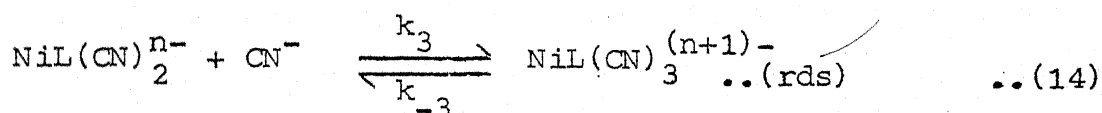
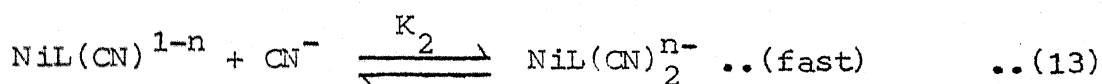
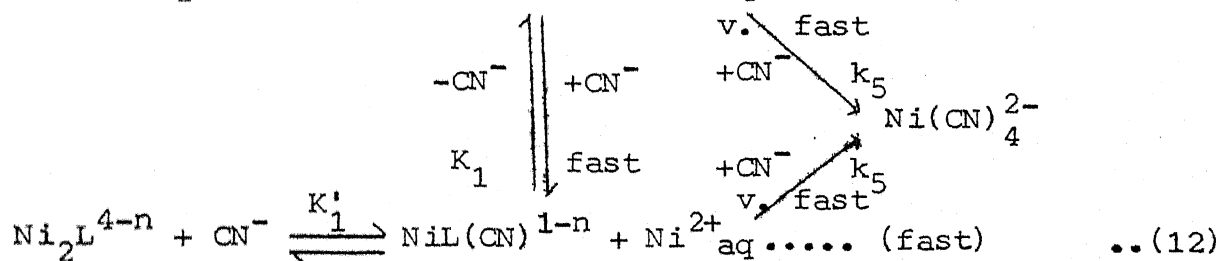
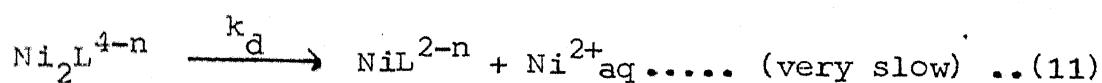


Fig. II.6 Resolution of the rate constants  $k_{\text{HCN}}$  and  $k_{\text{CN}}$  for the reaction of  $\text{Ni}_2\text{EGTA}$  with cyanide ion, (conditions as given in Table II.5)

## II.5 DISCUSSION

The initial part of the reaction of cyanide with the binuclear chelate  $\text{Ni}_2\text{EGTA}$  proceeds via two paths: (i) a slow dissociation and (ii) a fast cyanide assisted dissociation of  $\text{Ni}_2\text{L}$ . The following scheme out lines the proposed mechanism on the basis of experimental results and is in line with the mechanism proposed by us earlier<sup>17,18</sup>



The backward reaction rate depends upon the concentration of  $\text{Ni}(\text{CN})_4^{2-}$  and EGTA, and is inversely proportional to the free cyanide concentration. A steady state treatment<sup>21</sup> on the intermediate species  $\text{NiL}(\text{CN})_3$ ,  $\text{NiL}(\text{CN})_2$ ,  $\text{NiL}(\text{CN})$  and  $\text{NiL}$  and a consideration of dissociation of  $\text{Ni}_2\text{L}$  according to equation (11) gives a combined rate expression (equation 16)

$$\text{rate} = k_d [\text{Ni}_2\text{L}] + \frac{K'_1 K_2 k_3 [\text{CN}^-]^3 [\text{Ni}_2\text{L}]}{1 + K'_1 [\text{CN}^-] + K'_1 K_2 [\text{CN}^-]^2} \dots \text{..(16)}$$

which is easily transformed to the experimental rate expression given in equation (3).

The above expression shows that a third order dependence in cyanide would be expected if the reactant is  $\text{Ni}_2\text{L}$ . However only a first order dependence has been observed in the present study (Fig. II.3) though a first order dependence was observed for  $\text{Ni}_2\text{DTPA}$  and second order for  $\text{Ni}_2\text{TTHA}$  reactions in an earlier investigation<sup>18</sup>. No third order dependence has been seen so far. These results are interpreted to mean that only  $\text{NiL}(\text{CN})_2$  and  $\text{NiL}(\text{CN})$  are reactants consistent with first and second order dependences in cyanide. Accordingly the rate expression (16) is rewritten as

$$\text{rate} = k_d [\text{Ni}_2\text{L}] + k_f [\text{CN}^*]^{3-x} [\text{NiL}(\text{CN})_x]^{2-n-x} \quad \dots (17)$$

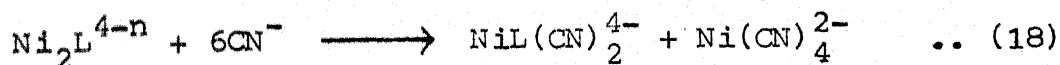
where  $x$  may be 1 or 2 and  $k_f$  is  $K_2k_3$  or  $k_3$  respectively. In the case of substitution reactions of mononuclear complexes of aminocarboxylates it has been shown that  $x$  can be 0, 1 and 2 corresponding to the observed third, second and first order dependences at low, medium and high concentration of cyanide. The zero order dependence in cyanide in the present case (Fig. II.3) points to a cyanide independent dissociation pathway for  $\text{Ni}_2\text{L}$  with a rate constant  $k_d$ .

In the pH range 7.5 to 9, the forward reaction is predominantly carried by a path that has one  $\text{HCN}$  and two  $\text{CN}^-$  molecules as reactants. A function  $\alpha_{\text{CN}}$  is defined as  $\alpha_{\text{CN}} = K_a / (K_a + [\text{H}^+])$ ,



where  $K_a$  is the dissociation constant of HCN. When  $k_f / \alpha_{\text{CN}}$  is plotted against  $\alpha_{\text{CN}}$ , a straight line is obtained (Fig. II.7), which shows that one molecule of HCN is involved in addition to two cyanides upto the rate determining step. The rate constants due to reactions of  $\text{CN}^-$  and HCN have been resolved and the solid line in Fig. II.5 gives the calculated curve using the resolved rate constants due to  $\text{CN}^-$  and HCN. The agreement between the experimental points and the calculated solid curve can be considered good.

A large absorbance change is observed after mixing the reactants (i.e.  $\text{Ni}_2\text{L}$  and cyanide) as a result of formation of  $\text{Ni}(\text{CN})_4^{2-}$  not from displacement of EGTA from  $\text{Ni}_2\text{EGTA}$  but from cyanide assisted dissociation of  $\text{Ni}_2\text{EGTA}$  according to equation (12) and rapid formation of  $\text{Ni}(\text{CN})_4^{2-}$  from  $\text{Ni}^{2+}(\text{aq})$ . Thereafter the reaction follows steps 13-15. The observed absorbance jump equals that expected from Beer's law and stoichiometric conversion according to equation (18).



The rather small activation energy ( $E_a = 6.1 \text{ kcal mol}^{-1}$ , Table II.4) determined from a temperature dependence study of the forward reaction where cyanide dependence is one, shows an associative mechanism to be operative in which bond breaking and bond making are taking place simultaneously. This value is comparable to that of other mono (amino carboxylato) nickel(II) reactions with  $\text{CN}^-$  investigated earlier<sup>1-4</sup>.

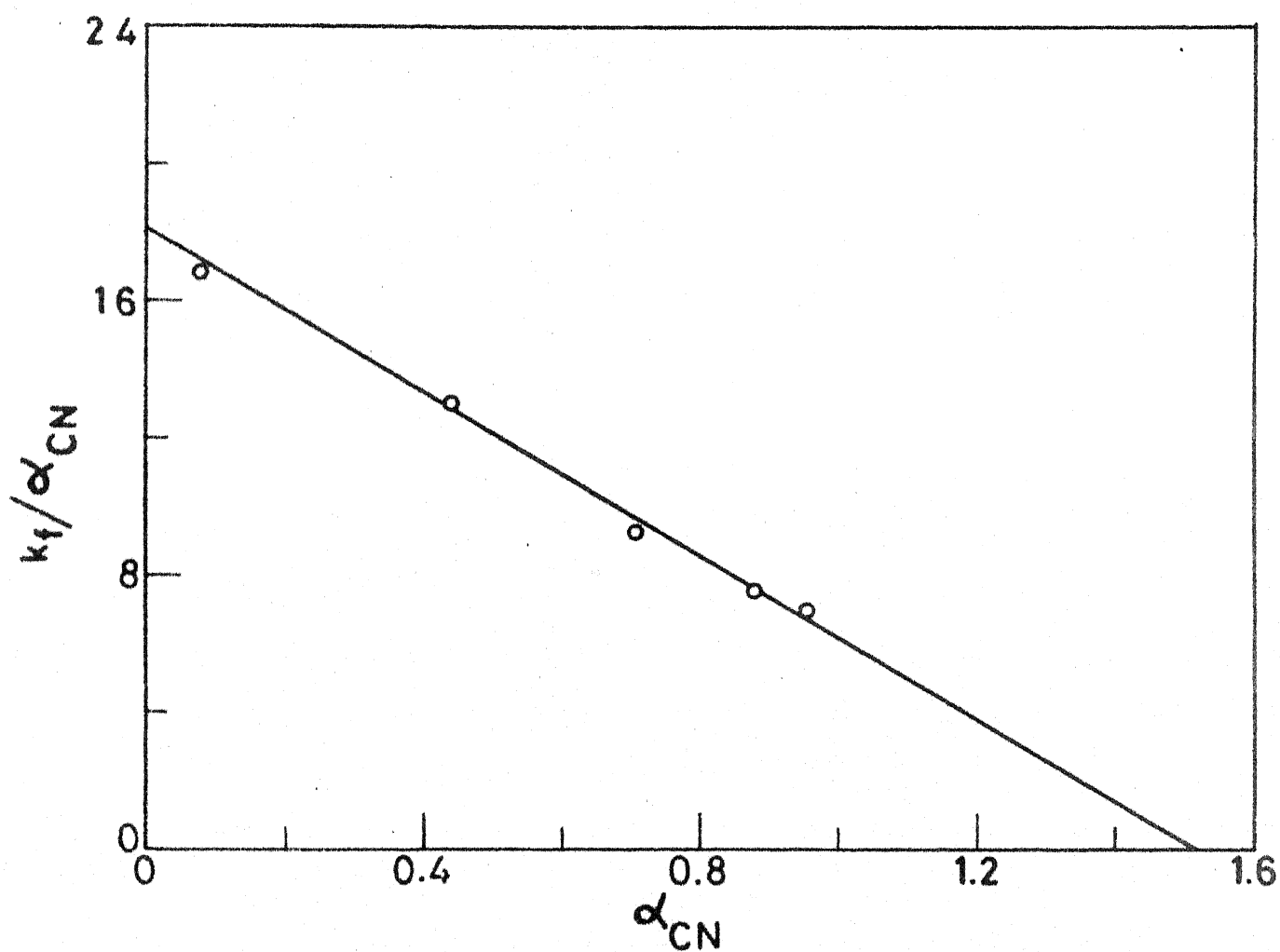


Fig.11.7 Plot of  $k_f/\alpha_{\text{CN}}$  Vs  $\alpha_{\text{CN}}$ , where  $\alpha_{\text{CN}} = K_a/([H^+] + K_a)$  and  $K_a$  is the dissociation constant of HCN.

Kinetic investigations on the reactions of some bis complexes of aminocarboxylates<sup>7</sup> and polyamines<sup>23</sup> with cyanide showed that the bis complexes first dissociate to give mixed complexes of the type  $\text{NiL}(\text{CN})_x$  which react further with excess cyanide to produce  $\text{Ni}(\text{CN})_4^{2-}$ .

The important steps in the reaction of cyanide ion with the binuclear nickel complex are the cyanide independent and cyanide assisted dissociation of the binuclear complex according to equations 11 and 12, followed by its conversion from an octahedral to a square planer complex via a penta coordinated intermediate as proposed earlier<sup>1-4</sup>. Three cyanides are required around the central nickel ion to bring about the rate determining step. The fourth cyanide adds rapidly displacing the remaining glycinate segment of the amino carboxylate to give the product. At pH values lower than 9, however, HCN is also a reactant along with  $\text{CN}^-$  in the rate determining step (Eq. 14) and an intra molecular transfer of proton seems to take place from HCN. Similar proton transfer was postulated in earlier studies also<sup>1-5,18</sup>. For the sake of comparison, the various rate constants and equilibrium constants evaluated for reactions of binuclear complexes of nickel(II) and TTHA, DTPA and EGTA with cyanide are tabulated in Table II.6.

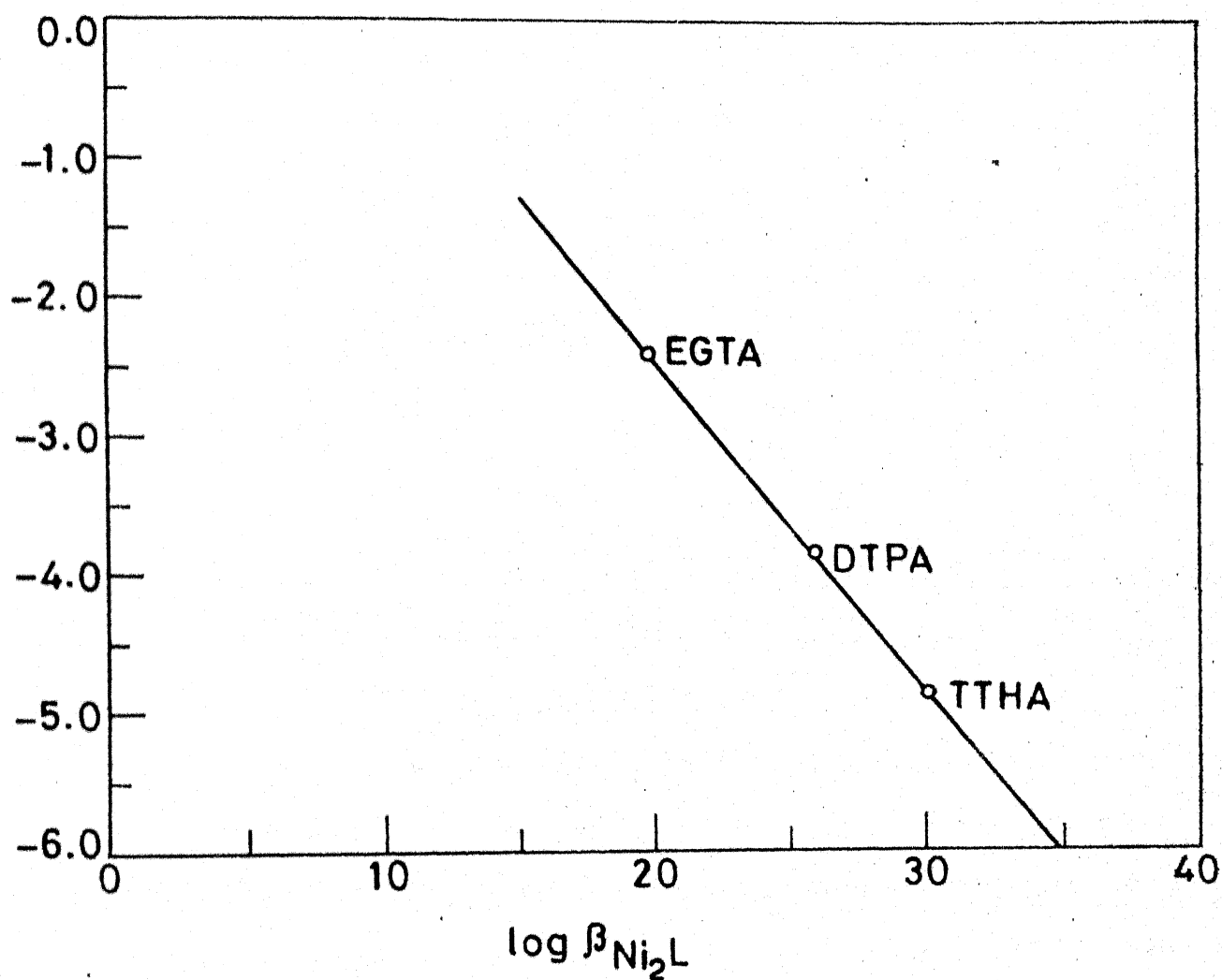
Table II.6. Summary of the rate constants and equilibrium constants

	Ni <sub>2</sub> TTHA	Ni <sub>2</sub> DTPA	Ni <sub>2</sub> EGTA
$K_{NiL}^{NiL}$	$1.0 \times 10^{13}$	$3.39 \times 10^5$	$7.94 \times 10^{-4}$
$\beta_{Ni_2L}^{Ni}$	$2.51 \times 10^{32d}$	$5.02 \times 10^{25d}$	$3.16 \times 10^{18d}$
$k_d, s^{-1}$	$(1.63 \pm 0.03) \times 10^{-5}$	$(1.40 \pm 0.05) \times 10^{-4}$	$3.9 \pm 0.4 \times 10^{-3}$
$k_3, M^{-1}s^{-1}$	-	$(1.63 \pm 0.05) \times 10^{-1}$	$8.1 \pm 0.5$
$K_2 k_3, M^{-2}s^{-1}$	$(10.15 \pm 1.40)$	-	-
$k_{CN}$	$10.15^a$	$1.77 \times 10^{-1b}$	$7.80^b$
$k_{HCN}$	$2.4^a$	$8.60 \times 10^{-2b}$	$3.5 \times 10^{-1b}$
$K_4^{-1} k_{-3}, s^{-1}$	$(3.08 \pm 0.17) \times 10^{-7c}$	$(4.78 \pm 0.6) \times 10^{-8c}$	$(7.1 \pm 0.5) \times 10^{-8}$

(a)  $M^{-2}s^{-1}$ ; (b)  $M^{-1}s^{-1}$ ; (c) from ref. 18; (d) ref. 22.

An interesting though not unexpected result is a linear correlation between  $\log \beta_{Ni_2L}^{Ni}$  and  $\log k_d^{Ni_2L}$  (Fig. II.8). This shows that the rate of dissociation at low cyanide concentration is inversely related to the overall stability of the binuclear complex.

A consideration of structures of binuclear complexes may be in order in so much as the structures of Ni<sub>2</sub>TTHA and Ni<sub>2</sub>DTPA



8 A Linear Free Energy Relationship : Plot of  $\log k_d^{Ni_2L}$  vs  $\log \beta_{Ni_2L}$ .

are known<sup>24</sup>. In each case one of the nickels is surrounded identically by two amine nitrogens and three carboxylate oxygens. In TTHA complex, the second nickel is bonded to two amines and three carboxylate groups, while in DTPA complex it is linked to one amine and two carboxylate groups. The latter is expected to be more labile to self dissociation than the former based on the idea of lesser number of binding sites. A correlation has been suggested<sup>25</sup> between electron donation abilities of multi-dentate ligand L in MAL type of complexes (M = Nickel, A = 5-nitro-salicylic acid and L = aminocarboxylates or polyamines) and their dissociation rates for the loss of 5-nitro salicylic acid. But here we are dealing with the case of a part of the multi-dentate ligand itself leaving one of the metal ions in a binuclear complex. The donating abilities of the three ligands can be estimated assuming additivity of  $E'_n$ 's (electron donor constants) of  $\text{NH}_3$  and  $\text{CH}_3\text{COOH}$  (1.84 and 0.95 respectively)<sup>25</sup>. The electron donating capacity for TTHA, DTPA and EGTA in the binuclear complexes can be calculated. TTHA has four amine nitrogens and six carboxylate groups, so its  $E'_n$  value is equal to  $4 \times 1.84 + 6 \times 0.95$  13.06. Similar calculations can be made for DTPA and EGTA.

For DTPA, which has three amine nitrogens and five carboxylate groups  $E'_n = 10.27$  and for EGTA,  $E'_n = 7.84$  with two amine nitrogens and four carboxylate groups. A log-log plot of  $E'_n$ 's vs  $k_d^{\text{Ni}_2\text{L}}$ , the dissociation rate constants of step given in equation (11) in the scheme, is found to be linear with a

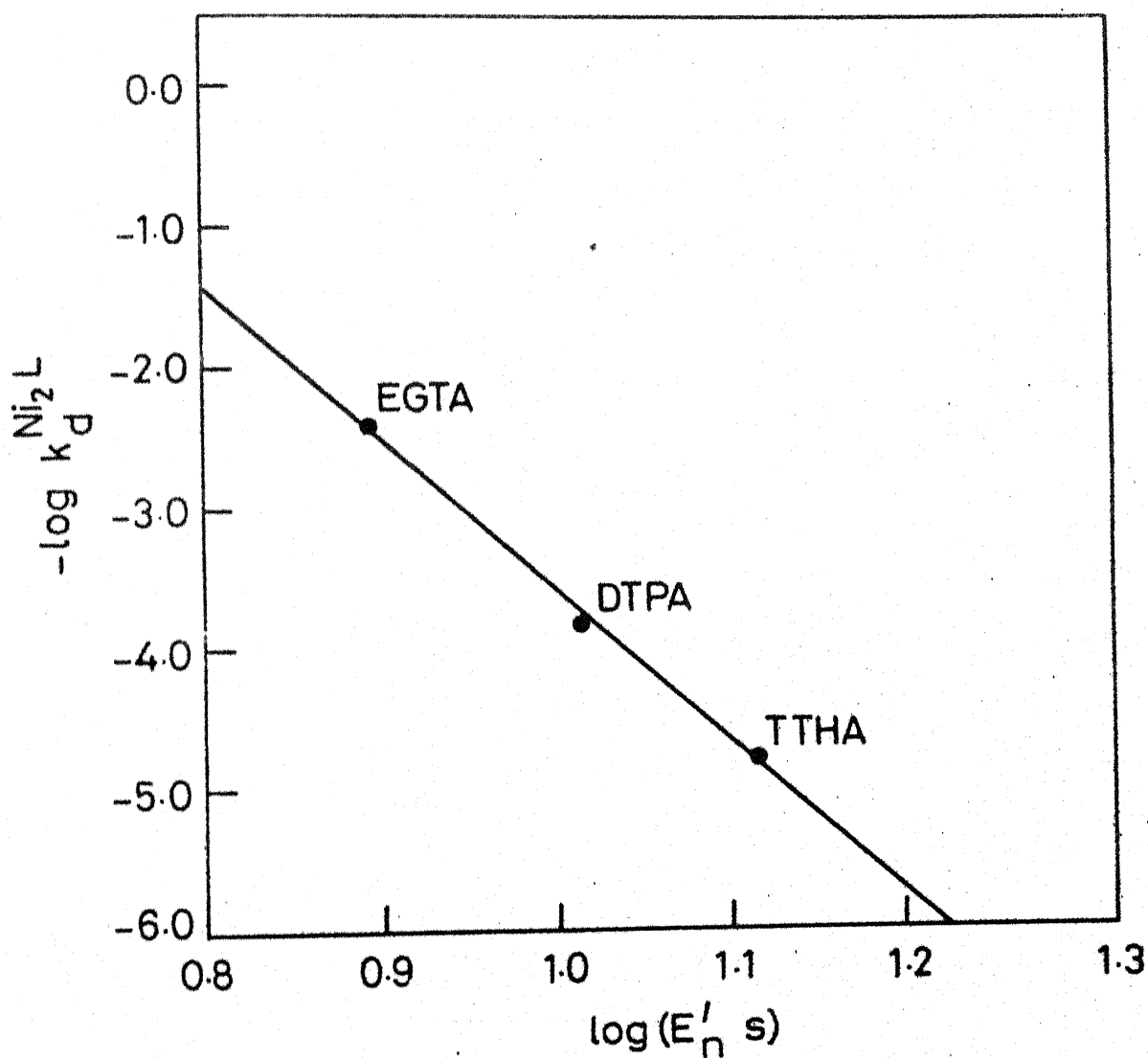
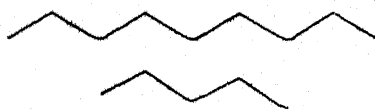


Fig. II-9 A log-log plot between  $k_d^{\text{Ni}_2\text{L}}$  and  $E'_n \text{ s}$  (Electron-donating capacities of Ligands.)

negative slope (Fig. II.9). This trend indicates that the lability of binuclear complexes towards self dissociation is inversely related to  $E'_n$ 's of the complexed ligands. The same is also reflected in the inverse linear relationship between  $\log \beta_{Ni_2L}^{Ni}$  and  $\log k_d^{Ni_2L}$  in Fig. II.8.





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### CHAPTER III

#### KINETICS AND MECHANISM OF TETRACYANO- NICKELATE(II) FORMATION FROM BIS(DI- ETHYLENE TRIAMINE) AND BIS (ETHYLENE DIAMINE) NICKEL(II) COMPLEXES

#### ABSTRACT

The kinetics and mechanism of formation of tetracyano-nickelate(II) from bis (diethylenetriamine)nickel(II) and bis ( ethylenediamine)nickel(II) has been studied in aqueous solution at 25°C using the stopped flow technique. The reaction is first order in bis complex and has a variable order dependence in cyanide from zero at low cyanide concentration changing to one at higher cyanide concentration. The rate expression has the form

$$\text{rate} = \left\{ k_d^{\text{NiL}} + k' [\text{CN}^-] \right\} [\text{NiL}_2]$$

which indicates that the bis complex is not directly converted into  $\text{Ni}(\text{CN})_4^{2-}$  but first loses one ligand molecule and

cyanide ion assists this loss. The reverse reaction between  $\text{Ni}(\text{CN})_4^{2-}$  and L, where L is diethylenetriamine (dien) or ethylenediamine (en) is first order in each reactant and inverse first order in cyanide. This shows that three cyanides are involved in the rate determining step. A possible mechanism is proposed which involves the successive displacement of the chelated amino groups by cyanide ions through the formation of a series of mixed ligand complexes. The difference in the kinetic behaviour of  $\text{Ni}(\text{dien})_2$  and  $\text{Ni}(\text{en})_2$  is explained.

### III.1 INTRODUCTION

The mechanism of formation and dissociation reactions of some complexes of polyamines with Ni(II) have been investigated previously<sup>1-5</sup>. Ligand exchange reactions involving nickel-polyamines, aminocarboxylates<sup>6</sup>, bipyridyl, 1,10 phenanthroline, and 2,2',2'' terpyridyl<sup>7</sup> have been studied extensively. A considerable amount of data is now available for the formation of  $\text{Ni}(\text{CN})_4^{2-}$  from Ni(II) chelates of aminocarboxylates<sup>8</sup>, polyamines<sup>9</sup>, phen<sup>10</sup> and  $\text{Ni}^{2+}(\text{aquo})$ <sup>11,12</sup>. Crouse and Margerum<sup>13</sup> have studied the reaction of  $\text{Ni}(\text{CN})_4^{2-}$  with various polyamines in presence and in absence of  $\text{I}_2$  as a scavenger for cyanide ion. In presence of  $\text{I}_2$ , the released cyanide has no effect on the forward reaction rate, but in absence of  $\text{I}_2$  there is an inverse effect.

In the present study the kinetics of the reaction of cyanide ion with two bis complexes of nickel(II),  $\text{NiL}_2$  where L is dien or en, have been reported.

### III.2 EXPERIMENTAL

Diethylene triamine obtained from Eastman Kodak Co. (U.S.A.) and ethylenediamine (B.D.H., India) were distilled under reduced pressure and stored in amber coloured bottles in dark. Their solutions in double distilled water were standardised potentiometrically with HCl. Bis complexes of nickel with dien and en were prepared by mixing stoichiometric amounts of standardised aqueous solutions of metal and ligand at appropriate pH. The concentration of bis complex was found spectrophotometrically as  $\text{Ni}(\text{CN})_4^{2-}$  by adding excess cyanide to the bis complex and noting the absorbance at 267 nm or 285 nm. All other reagents were of AR grade. Double distilled water was used to prepare all solutions.

A stopped flow spectrophotometer model SF-3A from Hitech, England, having a cell of 2 mm pathlength was used for study of the rapid reactions. An ECIL storage oscilloscope model OS 768-S equipped with a polaroid camera was used to record the kinetic traces. A Toshniwal Spectrophotometer Model RL-02 was used to study the slow reactions. The spectrophotometer used was equipped with a thermostated cell compartment. All pH measurements were made on an Elico digital pH meter Model LI-120 using BDH standard buffer solutions for standardization.

### III.3 KINETIC MEASUREMENTS

The exchange reactions of  $\text{NiL}_2$  with cyanide were followed by monitoring the concentration of  $\text{Ni}(\text{CN})_4^{2-}$  at 267 nm ( $\epsilon_{\text{Ni}(\text{CN})_4^{2-}}^{267} = 1.16 \times 10^4$ ) or at 285 nm ( $\epsilon_{\text{Ni}(\text{CN})_4^{2-}}^{285} = 4.63 \times 10^3$ ) where absorbance of  $\text{Ni}(\text{dien})_2$  and  $\text{Ni}(\text{en})_2$  were negligible at the concentration levels used for kinetic runs. The forward reactions were run in presence of excess cyanide and all gave good pseudo first order plots. The rate expression in the presence of excess cyanide is given by equation (1)

$$\frac{d[\text{Ni}(\text{CN})_4^{2-}]}{dt} = k_{\text{obsd}} [\text{NiL}_2]_T \quad \dots (1)$$

Where  $[\text{NiL}_2]_T$  includes the concentration of rapidly formed mixed cyanide complexes of the type  $\text{NiL}(\text{CN})_x$ .

### III.4 RESULTS

#### III.4.1 Reaction of $\text{Ni}(\text{dien})_2^{2+}$ with cyanide ion:

The rate of formation of  $\text{Ni}(\text{CN})_4^{2-}$  is first order each in  $\text{Ni}(\text{dien})_2$  and  $\text{CN}^-$  at pH 11.0 when cyanide is present in excess. The effect of variation of cyanide can be seen in Table III.1. The slope of a plot of  $\log(k_{\text{obsd}})$  vs  $\log[\text{CN}^-]_T$  (Fig. III.1) gives the order of reaction in cyanide.  $[\text{CN}^-]_T$  refers to total cyanide concentration including a small fraction of HCN present in the working pH range. The order in cyanide varies from zero at low cyanide concentration to one at higher cyanide concentration.

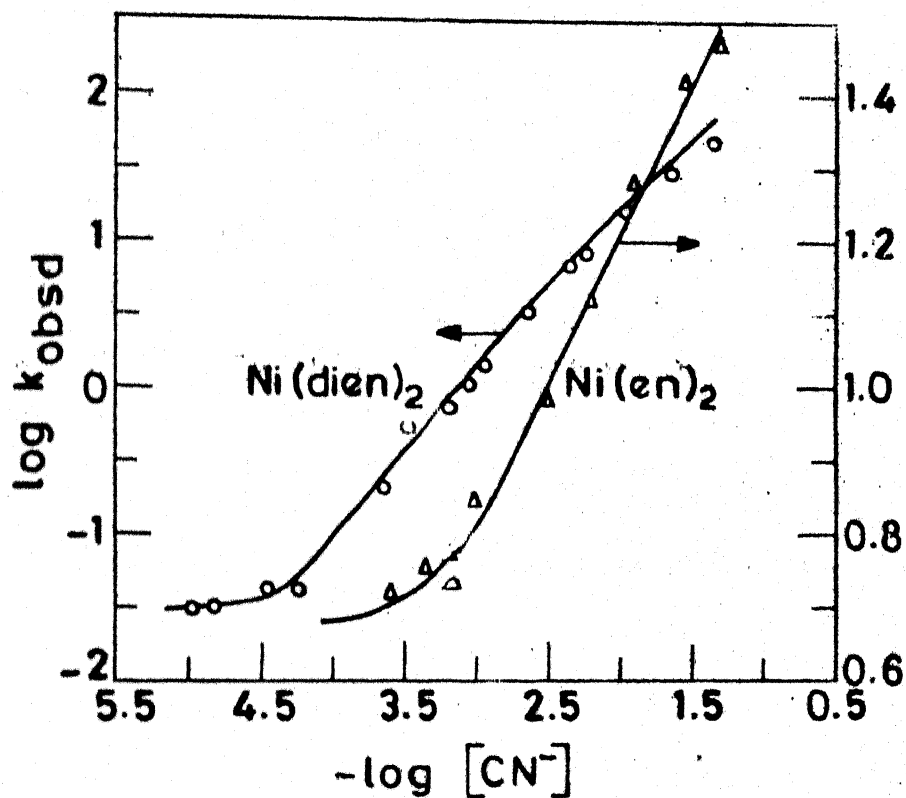


Fig.III.1 Cyanide dependence of the observed forward rate constants in the reaction of  $\text{Ni}(\text{dien})_2^{2+}$  and  $\text{Ni}(\text{en})_2^{2+}$  with cyanide ion. temp. =  $25^\circ\text{C}$ , pH = 11.0, and  $I = 0.1\text{M}$

Table III.1. Cyanide dependence for  $\text{Ni}(\text{dien})_2\text{-CN}^-$  Reaction

$$[\text{Ni}(\text{dien})_2^{2+}] = 6.1 \times 10^{-6} - 4.5 \times 10^{-5} \text{M}, \text{pH} = 11.0 \pm 0.1,$$

$$I = 0.1\text{M}, \text{temp.} = 25^\circ \pm 0.1^\circ\text{C}.$$

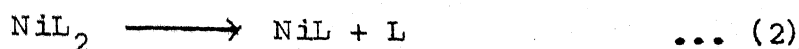
$[\text{CN}^-]_{\text{T}}, \text{M}$	$k_{\text{obsd}}, \text{s}^{-1}$	$10^{-3} \times k_f (= k_{\text{obsd}} / [\text{CN}^-]_{\text{T}})$
$4.44 \times 10^{-2}$	$50 \pm 2.0$	1.13
$2.22 \times 10^{-2}$	$30 \pm 0.5$	1.35
$1.11 \times 10^{-2}$	$16.4 \pm 0.5$	1.48
$5.55 \times 10^{-3}$	$8.2 \pm 0.5$	1.48
$4.44 \times 10^{-3}$	$6.8 \pm 0.5$	1.53
$2.22 \times 10^{-3}$	$3.2 \pm 0.2$	1.44
$1.11 \times 10^{-3}$	$1.4 \pm 0.2$	1.26
$8.88 \times 10^{-4}$	$1.1 \pm 0.15$	1.24
$6.66 \times 10^{-4}$	$0.7 \pm 0.04$	1.16
$4.44 \times 10^{-4}$	$0.6 \pm 0.05$	1.35
$2.22 \times 10^{-4}$	$0.042 \pm 0.003^*$	-
$5.77 \times 10^{-5}$	$0.037 \pm 0.002^*$	-
$3.45 \times 10^{-5}$	$0.035 \pm 0.002^*$	-
$7.8 \times 10^{-5}$	$0.04 \pm 0.003^*$	-

\* Zero order dependence in cyanide.

This observation was also reported by Margerum et al.<sup>14</sup> while studying the reaction of cyanide ion with bis complexes of IDA and MIDA of nickel(II). The observed zero order dependence in cyanide indicates a slow dissociation step according to



equation (2) followed by further reaction of NiL with cyanide to give  $\text{Ni}(\text{CN})_4^{2-}$  finally.



Thus  $k_{\text{obsd}}$  can be expressed by equation (3)

$$k_{\text{obsd}} = k_{\text{d}}^{\text{NiL}} 2 + k_3 [\text{CN}^-] \quad \dots (3)$$

The values of  $k_{\text{d}}^{\text{NiL}} 2$  and  $k_3$  thus obtained are  $3.85 \times 10^{-2} \text{ s}^{-1}$  and  $1.34 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  respectively.

#### III.4.2 Dependence of forward rate on pH for $\text{Ni}(\text{dien})_2\text{-CN}^-$ reaction:

The pH of the reaction medium was varied from 8.2-11.0 and it was found that the reaction rate increases with an increase of pH and then levels off at pH above 9.5 (Table III.2, Fig. III.2). The pH values were corrected for  $-\log [\text{H}^+]$  by subtracting 0.11 from recorded pH values<sup>15</sup>. The increase in rate on increase of pH can be accounted for by the difference in reactivities of cyanide and HCN as nucleophiles. The rates due to  $\text{CN}^-$  and HCN can be resolved as follows:

$$k_f [\text{CN}^-]_{\text{T}} = k_{\text{CN}} [\text{CN}^-] + k_{\text{HCN}} [\text{HCN}] \quad \dots (4)$$

$$= \{k_{\text{CN}} + k_{\text{HCN}} K_{\text{HCN}} [\text{H}^+]\} [\text{CN}^-]$$

$$\text{or } k_f \frac{[\text{CN}^-]_{\text{T}}}{[\text{CN}^-]} = k_{\text{CN}} + k_{\text{HCN}} K_{\text{HCN}} [\text{H}^+] \quad \dots (5)$$

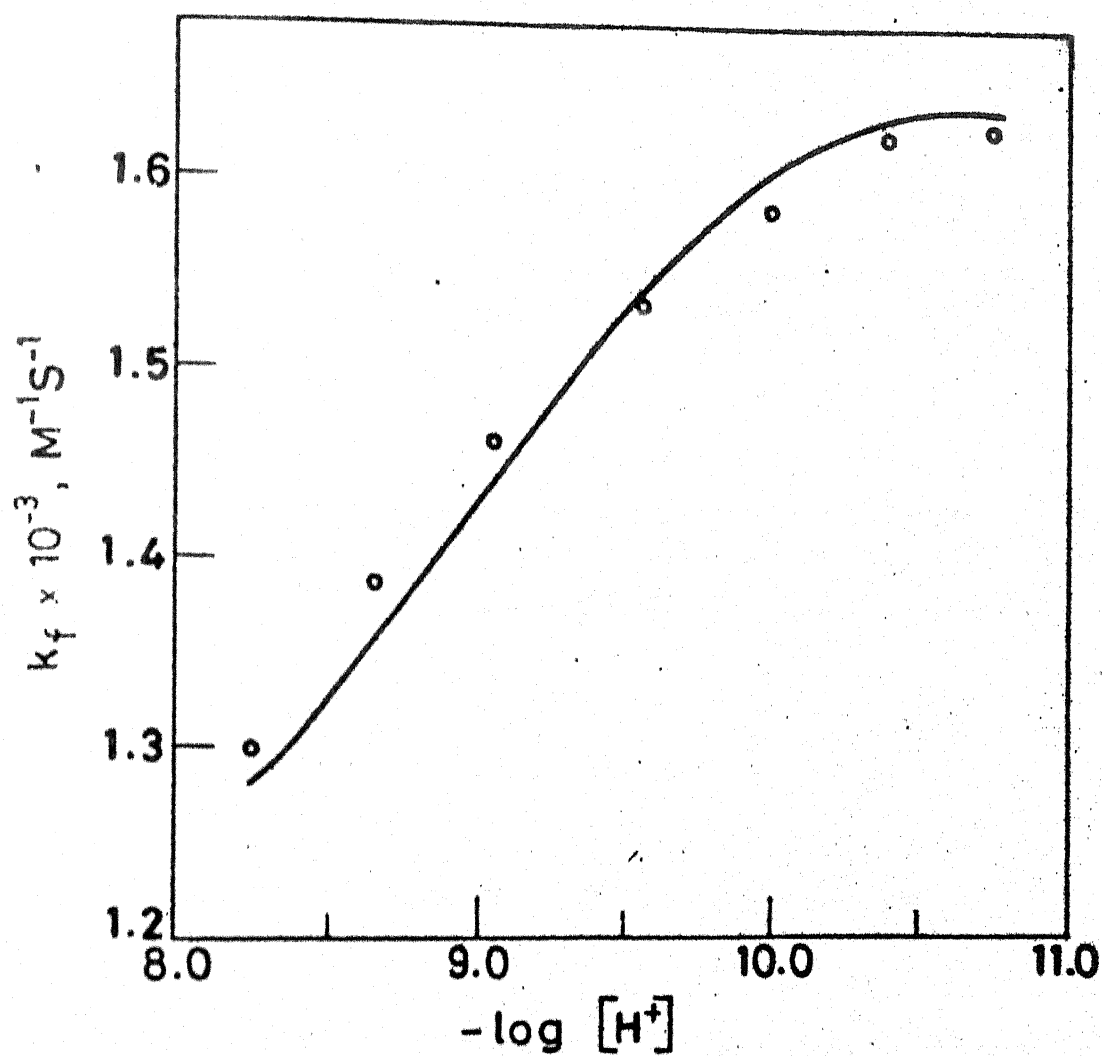


Fig.III.2 Effect of pH on the reaction of  $\text{Ni(dien)}_2^{2+}$  with cyanide. temp.  $\approx 25^\circ\text{C}$ , and  $I = 0.1\text{M}$ .

where  $[\text{CN}^-]_{\text{T}} / [\text{CN}^-] = 1 + K_{\text{HCN}} [\text{H}^+]$  and  $K_{\text{HCN}}$  is the protonation constant of  $\text{CN}^-$  ( $\log K_{\text{HCN}} = 9.0$  at  $I = 0.1$ ,  $\text{temp.} = 25^\circ\text{C}$ ).

Thus a plot of left hand side of equation (5) ~~vs.~~  $[\text{H}^+]$  gives a straight line (Fig. III.3) and from the slope and intercept of this line, both  $k_{\text{HCN}}$  and  $k_{\text{CN}}$  can be calculated. Their respective values are  $1.25 \times 10^{-3} \text{ M}^{-1}\text{S}^{-1}$  and  $1.65 \times 10^{-3} \text{ M}^{-1}\text{S}^{-1}$ .

Table III.2. Effect of pH on the forward rate constant for the reaction of cyanide with  $\text{Ni}(\text{dien})_2^{2+}$ .

$[\text{Ni}(\text{dien})_2^{2+}]_{\text{T}} = 4.8 \times 10^{-5} \text{ M}$ ,  $[\text{CN}^-]_{\text{T}} = 2.22 \times 10^{-3} \text{ M}$   
 $\text{temp.} = 25^\circ \pm 0.1^\circ\text{C}$ ,  $I = 0.1\text{M}(\text{NaClO}_4)$ .

pH	$k_{\text{obsd}}, \text{S}^{-1}$
8.23	$2.9 \pm 0.3$
8.65	$3.1 \pm 0.15$
9.05	$3.3 \pm 0.1$
9.55	$3.4 \pm 0.1$
10.00	$3.5 \pm 0.05$
10.4	$3.5 \pm 0.2$
10.72	$3.5 \pm 0.2$

The solid line in Fig. III.2 is the calculated curve obtained by using these resolved rate constants. The agreement between theoretical curve and experimental points is reasonably good.

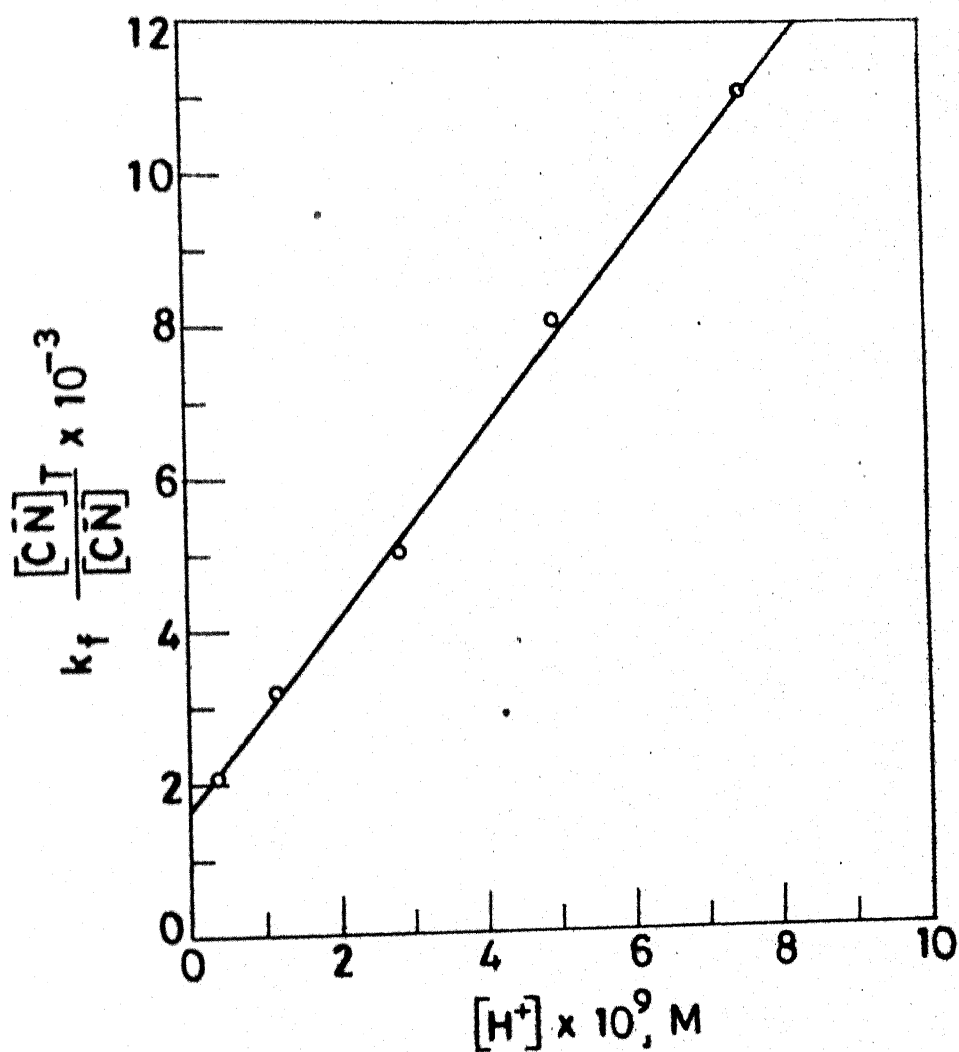


Fig. III.3 Resolution of rate constants for the reaction of  $\text{Ni}(\text{dien})_2^{2+}$  with cyanide ion.

### III.4.3 Reaction of $\text{Ni(en)}_2^{2+}$ with cyanide ion:

The observed reaction of bis (ethylene diamine) complex of nickel(II) with cyanide is first order in  $\text{Ni(en)}_2$  and the rate increases with increasing cyanide ion concentration (Table III.3, Fig. III.1). The nature of dependence on cyanide concentration shows that the bis complex dissociates slowly to

Table III.3. Kinetic Experiments at various cyanide concentrations for the reaction of cyanide ion with  $\text{Ni(en)}_2^{2+}$   
 $[\text{Ni(en)}_2^{2+}]_T = 1.6 \times 10^{-5} \text{M}$ ,  $\text{pH} = 11.0 \pm 0.1$ ,  $I = 0.1 \text{M} (\text{NaClO}_4)$ ,  
 $\text{temp.} = 25 \pm 0.1^\circ \text{C}$ .

$[\text{CN}^-]_T, \text{M}$	$k_{\text{obsd}}, \text{s}^{-1}$
$5.06 \times 10^{-2}$	$29.8 \pm 1.0$
$3.06 \times 10^{-2}$	$24.5 \pm 0.7$
$2.4 \times 10^{-2}$	$22.0 \pm 0.5$
$1.22 \times 10^{-2}$	$18.6 \pm 0.7$
$6.1 \times 10^{-3}$	$13.3 \pm 0.5$
$3.05 \times 10^{-3}$	$11.4 \pm 0.3$
$8.55 \times 10^{-4}$	$9.8 \pm 0.2$
$6.1 \times 10^{-4}$	$5.2 \pm 0.1$
$3.60 \times 10^{-4}$	$5.5 \pm 0.05$
$2.44 \times 10^{-4}$	$5.21 \pm 0.05$

the mono complex and this mono complex reacts rapidly with cyanide through the formation of mixed ligand complexes, finally giving  $\text{Ni}(\text{CN})_4^{2-}$ . In this case, if first order dependence in cyanide is assumed then

$$k_{\text{obsd}} = k_d^{\text{NiL}} 2 + k [\text{CN}^-]_T \quad \dots (6)$$

Rearranging the above expression we get

$$\frac{k_{\text{obsd}}}{[\text{CN}^-]_T} = \frac{k_d^{\text{NiL}} 2}{[\text{CN}^-]_T} + k \quad \dots (7)$$

thus a plot of  $\frac{k_{\text{obsd}}}{[\text{CN}^-]_T}$  vs  $\frac{1}{[\text{CN}^-]_T}$  should give a straight line which is found to be the case (Fig. III.4). Hence the stipulation about first order dependence in cyanide, made above is correct. The values of  $k_d^{\text{NiL}} 2$  and  $k$ , obtained from the slope and intercept of this plot, are  $5.1 \text{ s}^{-1}$  and  $1.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  respectively.

Unlike the case of bis complex of dien discussed before the values of  $k_d^{\text{NiL}} 2$  for ethylene diamine complex is quite high. This accounts for the slope for  $\text{Ni}(\text{en})_2$  being different than the expected value of one (Fig. III.1). However, a plot of  $\log (k_{\text{obsd}} - k_d^{\text{NiL}} 2)$  against  $\log [\text{CN}^-]$  is linear with a slope equal to one (Fig. III.5) confirming again the first order dependence in cyanide in case of en as well.

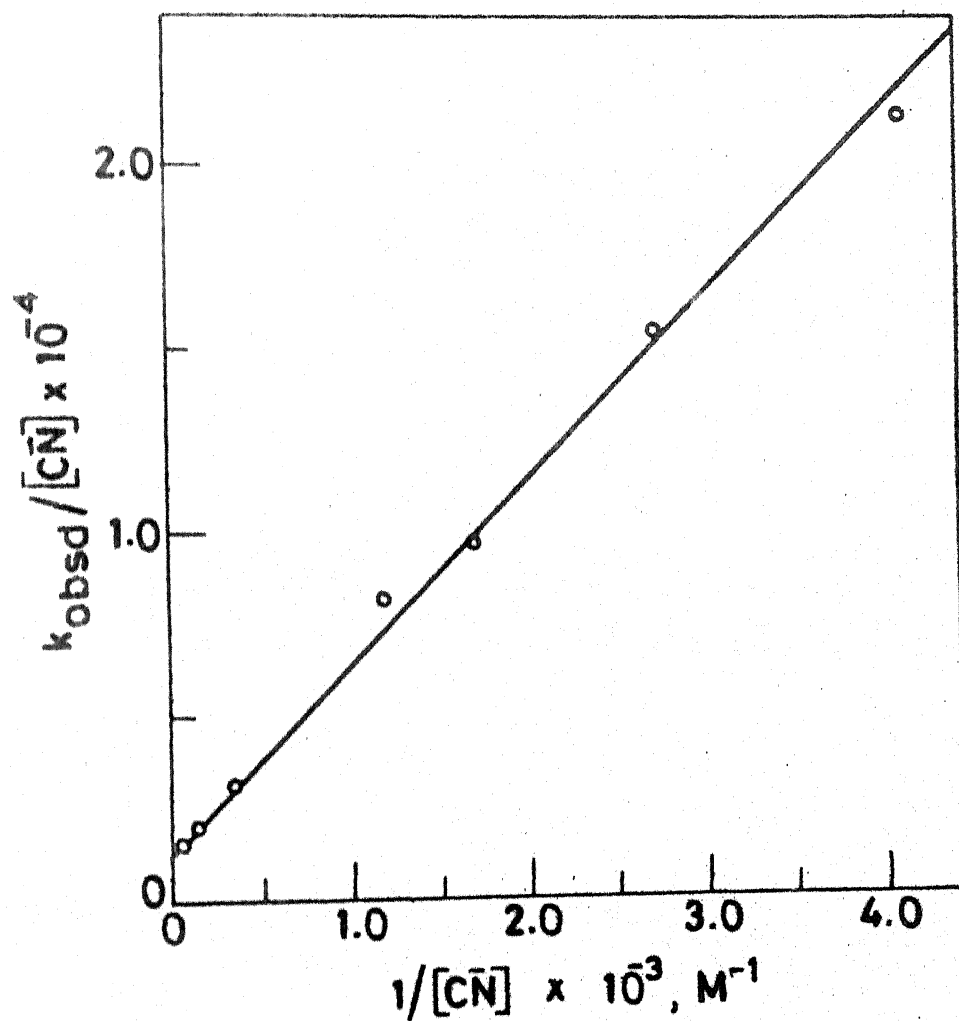


Fig. III.4 Plot of  $k_{\text{obsd}}/[\text{CN}^-]_{\text{T}}$  Vs  $1/[\text{CN}^-]_{\text{T}}$  for the reaction of  $\text{Ni}(\text{en})_2^{2+}$  with cyanide ion.

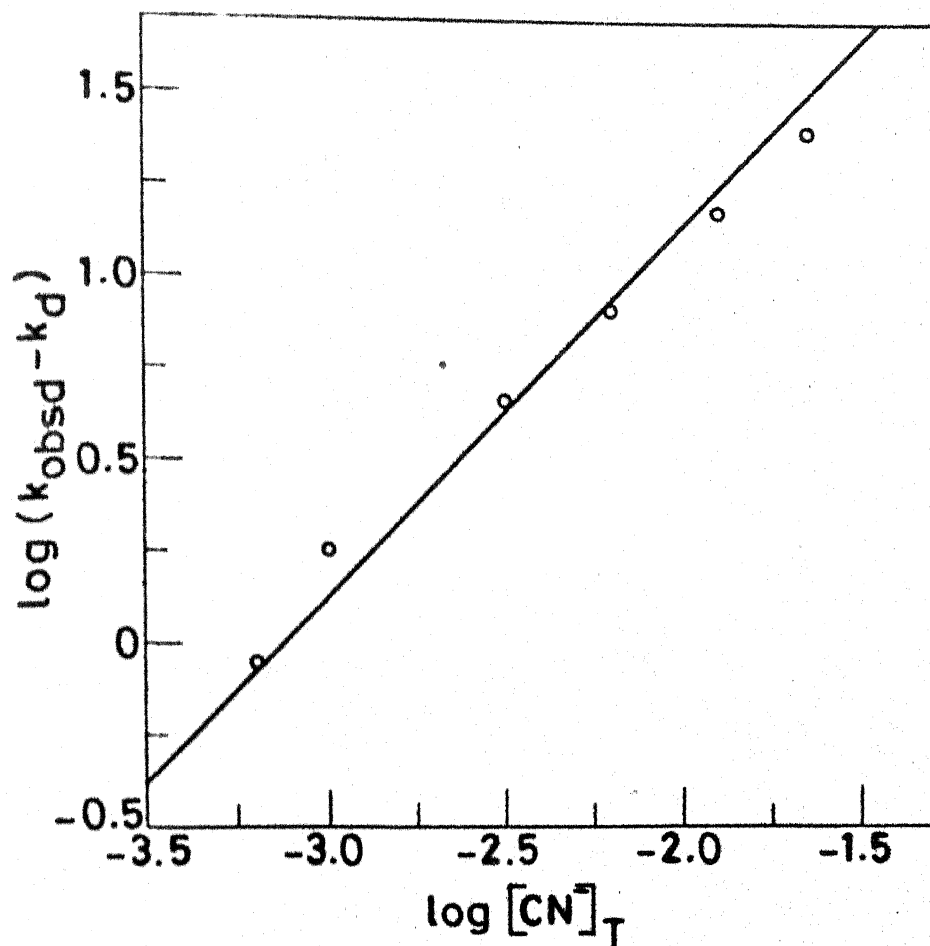


Fig.III.5 Plot of  $\log(k_{\text{obsd}} - k_d)$  Vs  $\log [\text{CN}^-]_T$   
for the reaction of  $\text{Ni(en)}_2^{2+}$  with cyanide  
ion



### III.4.4 Kinetics of Reverse Reactions

The disappearance of  $\text{Ni}(\text{CN})_4^{2-}$  is greatly accelerated by the presence of polyamines in comparison to the much slower reaction of  $\text{Ni}(\text{CN})_4^{2-}$  with aminocarboxylates<sup>6</sup> or perchloric acid<sup>7</sup>. The stability constants of nickel-polyamine complexes are smaller than  $\text{Ni}(\text{CN})_4^{2-}$ , therefore a large excess of polyamine is required to force the reverse reaction. A notable feature of the reverse reaction is an inverse first order dependence in cyanide. The integrated rate expression is formulated as equation (8)

$$(A_i - A_t) + A_i \ln \frac{A_t}{A_i} = - \frac{\epsilon l}{4} k'_{\text{obsd}} \cdot t \quad \dots (8)$$

where  $A_i$ ,  $A_t$ ,  $\epsilon$  and  $l$  have their usual meanings described elsewhere<sup>8</sup> and in Chapt. II,  $k'_{\text{obsd}} = k_r [L]_T$ . From the plots of left hand side of equation (8) vs  $t$ ,  $k'_{\text{obsd}}$  and hence  $k_r$  can be calculated from the slopes of above plots. The values of  $k_{\text{obsd}}$  and  $k_r$  are given in Table III.4.

Table III.4. Kinetics of decomposition of  $\text{Ni}(\text{CN})_4^{2-}$  in its reaction with dien & en.

#### A. Dien

$[\text{Ni}(\text{CN})_4^{2-}]_T = 2.6 \times 10^{-5}$ , pH = 11.0  $\pm$  0.1, I = 0.1M and temp. = 25°C

$[\text{Dien}]_T, \text{M}$	$k'_{\text{obsd}} \times 10^9, \text{M}^{-1} \text{s}^{-1}$	$10^6 \times k_r, \text{s}^{-1}$
1	2	3
$1.45 \times 10^{-3}$	6.96	4.76

1	2	3
$1.08 \times 10^{-4}$	5.28	4.86
$0.72 \times 10^{-4}$	3.67	4.97

$$A_v = 4.86 \pm 0.1 \times 10^{-6} \text{ s}^{-1}$$

#### B. EN

$[\text{Ni}(\text{CN})_4^{2-}]_T = 8.25 \times 10^{-5} \text{ M}$ , pH =  $11.0 \pm 0.1$ , I = 0.5M, temp. =  $25^\circ \text{C}$

$[\text{EN}]_T, \text{M}$	$k'_{\text{obsd}} \times 10^5, \text{M}^{-1} \text{s}^{-1}$	$10^4 \times k_r, \text{s}^{-1}$
$1.8 \times 10^{-1}$	5.8	3.2
$2.0 \times 10^{-1}$	7.4	3.7
$2.5 \times 10^{-1}$	8.5	3.4
$3.0 \times 10^{-1}$	9.6	3.2

$$A_v = (3.38 \pm 0.24) \times 10^{-4} \text{ s}^{-1}$$

#### III.4.5 Effect of Temperature

The activation parameters calculated from the Arrhenius plots for the forward and reverse reactions for both the reactions are given in Table III.5. The activation parameters for the forward reaction were determined for both situations i.e. where order with respect to cyanide is zero and one. An interpretation of these parameters is deferred to section on discussion.

Table III.5. Activation parameters for the forward and reverse reactions *per mole*.

A. Ni(dien)<sub>2</sub>-CN<sup>-</sup> System

Forward Reaction:

For zero order dependence  
in [CN<sup>-</sup>]

$$\begin{aligned} E_a &= 18.5 \text{ kcal} \\ \Delta H^\ddagger &= 17.9 \text{ kcal} \\ \Delta S^\ddagger &= -6.0 \text{ e.u.} \\ pZ &= 4.1 \times 10^{11} \text{ cm}^{-1} \end{aligned}$$

For first order dependence  
in [CN<sup>-</sup>]

$$\begin{aligned} &9.5 \text{ kcal} \\ &8.9 \text{ kcal} \\ &-14.5 \text{ e.u.} \\ &4.4 \times 10^9 \text{ cm}^{-1} \end{aligned}$$

Reverse Reaction

$$\begin{aligned} E_a &= 18.7 \text{ kcal} \\ \Delta H^\ddagger &= 18.1 \text{ kcal} \\ \Delta S^\ddagger &= -17.5 \text{ e.u.} \\ pZ &= 9.1 \times 10^8 \text{ cm}^{-1} \end{aligned}$$

B. Ni(en)<sub>2</sub>-CN<sup>-</sup> System

Forward Reaction:

$$\begin{aligned} E_a &= 10.7 \text{ kcal} \\ \Delta H^\ddagger &= 10.1 \text{ kcal} \\ \Delta S^\ddagger &= -19 \text{ e.u.} \\ pZ &= 4.1 \times 10^8 \text{ cm}^{-1} \end{aligned}$$

Reverse Reaction:

$$\begin{aligned} &16.5 \text{ kcal} \\ &15.9 \text{ kcal} \\ &-21.5 \text{ e.u.} \\ &1.32 \times 10^8 \text{ cm}^{-1} \end{aligned}$$

the mono complex reacts rapidly to form mixed cyanide complex  $\text{NiL}(\text{CN})_x$  (where  $x=2$ ). The addition of third cyanide is the rate determining step followed by the rapid addition of fourth cyanide to finally give  $\text{Ni}(\text{CN})_4^{2-}$ . Depending upon the structure and nature of leaving ligand and stability of mixed cyanide chelate formed, the formation of  $\text{NiL}(\text{CN})_2$  may be slow or fast equilibrium step. The observed first order dependence in cyanide (in addition to cyanide independent dissociation shown in Eqn.(9)) also leads one to conclude that  $k_{\text{CN}}^{\text{NiL}} 2$  may or may not be the slowest step. Thus experiments were carried out to find the slowest observed step for the bis complexes under study. The rate constant  $k_{\text{CN}}^{\text{NiL}} 2$  for cyanide assisted dissociation step calculated under conditions when  $[\text{NiL}_2]$  is in excess or comparable to  $[\text{CN}^-]$  (Table III.6) was found to be higher than that of experimentally observed rate constants at high cyanide concentrations in the case of reaction of  $\text{Ni}(\text{dien})_2^{2+}$  with cyanide ion

Table III.6. Forward Rate Constants in presence of excess  $\text{Ni}(\text{dien})_2$  at  $25^\circ\text{C}$ ,  $\text{pH} = 11.0$  and  $I = 0.1\text{M}$ .

$$[\text{Ni}(\text{dien})_2^{2+}]_T = 3.6 \times 10^{-3}\text{M}$$

$[\text{CN}^-]_T, \text{M}$	$10^{-4} \times k_{\text{CN}}^{\text{NiL}} 2, \text{M}^{-1}\text{s}^{-1}$
$3.55 \times 10^{-3}$	$6.6 \pm 0.6$
$3.33 \times 10^{-3}$	$7.1 \pm 0.7$
$1.06 \times 10^{-4}$	$6.9 \pm 1.0$
$\text{Av} = (6.8 \pm 0.7) \times 10^4$	

(Table III.1) indicating that the addition of third cyanide is the rate determining step for  $\text{Ni}(\text{dien})_2$ . Moreover, inverse first order dependence in cyanide for the backward reaction also confirms the supposition that the step shown in equation (12) is the rate determining step and  $k_r$  thus obtained is equated to  $k_4^{-1} k_3$ . Thus the reacting species for the forward reaction is  $\text{Ni}(\text{Dien})(\text{CN})_2$  and its stability must be quite high. If this were not so, at low cyanide concentration the complete conversion of  $\text{NiL}$  to  $\text{NiL}(\text{CN})_2$  would not have been possible. Values of  $K_1 K_2$  can be calculated from an expression derived earlier<sup>14</sup> and given below Eqn. 14).

$$K_1 K_2 = \frac{k_4^{-1} k_{-3} \beta_4}{k_3 K_{\text{NiL}}} \quad \dots (14)$$

where  $\beta_4$  is the overall stability constant of  $\text{Ni}(\text{CN})_4^{2-}$  ( $\log \beta_4 = 30.5^9$ ) and  $K_{\text{NiL}}$  is the stability constant of the mono complex. The value of product  $K_1 K_2$  thus calculated for  $\text{Ni}(\text{dien})(\text{CN})_2$  is  $9.5 \times 10^{+10} \text{ M}^{-1}$ . This value is quite high and suggests that the rapid and complete conversion of  $\text{Ni}(\text{dien})$  to  $\text{Ni}(\text{dien})(\text{CN})_2$  can be expected.

Using a similar treatment for  $\text{Ni}(\text{en})_2$  it was found that the magnitude of  $K_1 K_2$  is  $1.6 \times 10^{16} \text{ M}^{-1}$  which is many orders of magnitude higher than the maximum possible value estimated for  $\text{NiL}(\text{CN})_2$ . According to Margerum<sup>9</sup> the magnitude of stability constant of a ternary complex  $\text{NiL}(\text{CN})_2$  will be equal to or less than the stability constant of  $\text{Ni}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$  estimated to equal  $3 \times 10^{11}$ .<sup>9</sup> The large difference in stability calculated from

Eqn. (14) and the maximum estimated value given above shows that Eqn. (14), which is derived on the supposition that addition of third cyanide is rate determining, does not apply in the case of  $\text{Ni(en)}_2$ -cyanide system. In other words, the rate determining step for the forward reaction does not lie in Eqn. 12 as in case of reactions of  $\text{Ni(dien)}_2$  and  $\text{Ni(par)}_2^{16}$ . Thus for  $\text{Ni(en)}_2$ ,  $k_{\text{CN}}^{\text{NiL}_2}$  is small as compared to  $k_3$  and the rate determining step moves to Eqn. 10.

The effect of ionic strength on the rate makes it possible to decide further between the two choices of rate determining step. In Eqn. (12) where interaction is envisaged between a neutral species and cyanide ion, the effect of ionic strength on rate should be negligible. However, if the rate determining step involves reaction between charged  $\text{NiL}_2$  and  $\text{CN}^-$  as in Eqn. (10) a negative salt effect should be observed as seen in Table III.7.

Table III.7. Effect of ionic strength on the observed pseudo first order rate constant for the reaction of  $\text{Ni(en)}_2^{2+}$  with  $\text{CN}^-$  ion.

$$[\text{Ni(en)}_2^{2+}]_{\text{T}} = 9.2 \times 10^{-5} \text{M}, [\text{CN}^-]_{\text{T}} = 4.0 \times 10^{-3} \text{M},$$

$$\text{pH} = 11.0 \pm 0.15, \text{ temp.} = 25^\circ\text{C}.$$

I, M ( $\text{NaClO}_4$ )	$k_{\text{obsd}}, \text{s}^{-1}$
0.1	12.5
0.2	8.8
0.3	7.7
0.45	7.0

Therefore, it can be inferred that in case of  $\text{Ni(en)}_2$  reaction the cyanide assisted dissociation is rate determining in preference to the addition of third cyanide as in case of  $\text{Ni(dien)}_2$ .

A similar conclusion has been arrived at by Margerum et al. while studying the substitution reaction of  $\text{CN}^-$  with  $\text{Ni(IDA)}_2$  and  $\text{Ni(MIDA)}_2$ <sup>14</sup>. Nigam et al.<sup>16</sup> have studied the reaction of  $\text{Ni(Par)}_2$  with cyanide and have shown that the step involving  $k_3$  is rate determining.

The different behaviour of  $\text{Ni(en)}_2$  compared to  $\text{Ni(dien)}_2$  may be due to its bidentate nature and cis configuration of water in  $\text{Ni(en)}_2$  complex<sup>17</sup>. Hague et al.<sup>18</sup> observed that the ligands attached to a metal centre labilise the attached water molecule to a lesser extent when they are located at cis position than when they are present at trans position to the ligand. If this view is correct, the first addition of  $\text{CN}^-$  to  $\text{Ni(en)}_2$  involving the displacement of water molecule at cis position is expected to be slower than the addition of third cyanide when water may occupy a trans position to the attached ligand.

Interestingly the magnitude of  $K_1K_2$  for the reaction of cyanide with  $\text{Ni(Par)}_2$ <sup>16</sup> complex is reported to be  $2.1 \times 10^9$ , a value lower than that of the  $\text{Ni(dien)}_2$  complex. This may be due to the non labilising effect of the aromatic nature of Par ligand because polyamine nitrogens<sup>19,20</sup> appear to accerelate water loss whereas aromatic ones do not<sup>21,22</sup>.

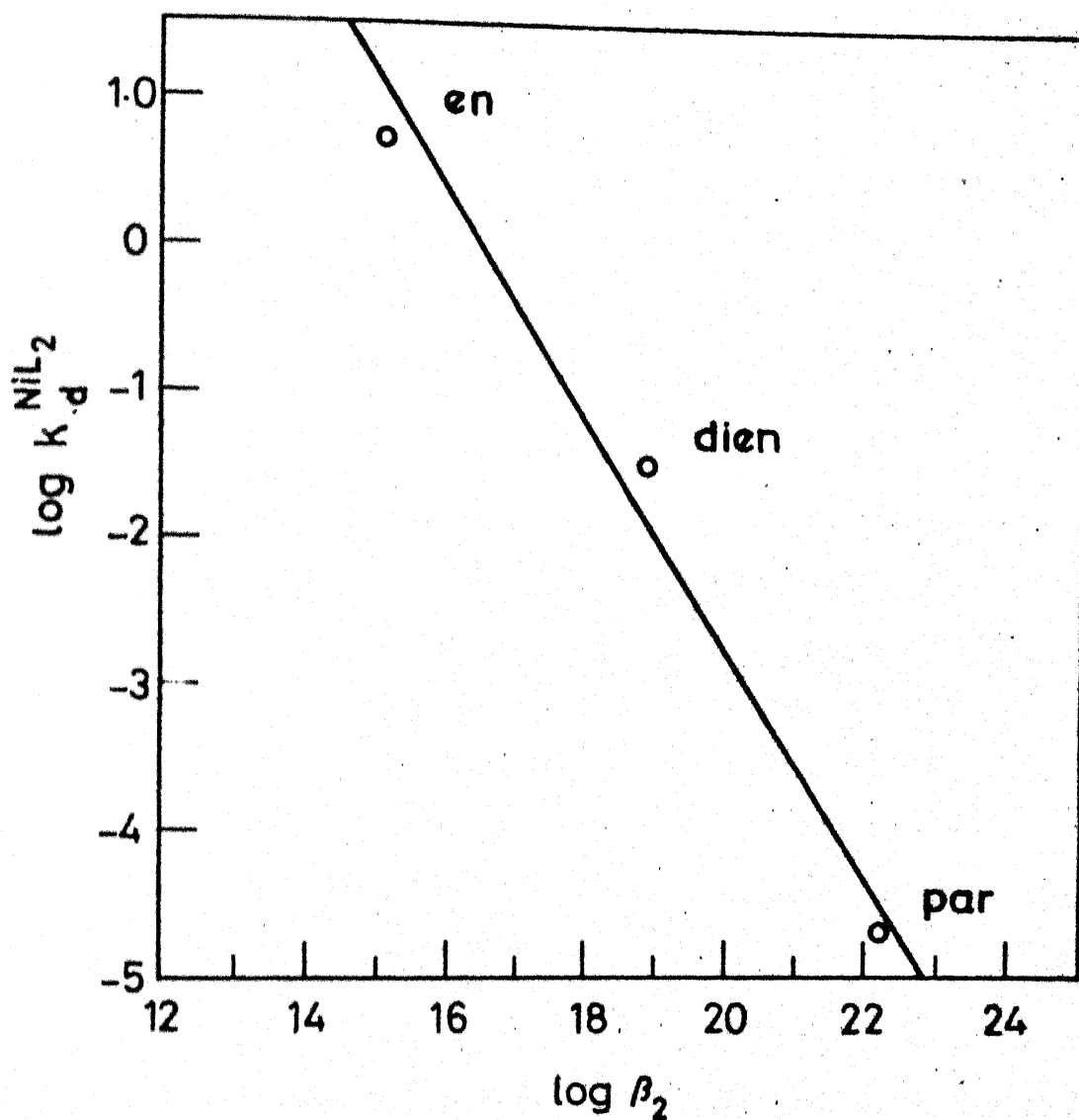


Fig. III-6 A Linear Free Energy Relationship (LFER); a plot of  $\log k_d^{NiL2}$  Vs  $\log \beta_2$ ,



The difference in activation energies of forward reaction for situations where order in cyanide is zero and one (Table III.5) indicates the occurrence of two different paths in two situations at different cyanide concentrations. The cyanide independent path is a dissociative one where bond breaking takes place and hence has a higher activation energy and correspondingly a less negative entropy change. On the other hand, cyanide assisted dissociation seems to be associative one and hence with low activation energy. The large negative entropy change for forward reaction at high cyanide concentration and also for reverse reaction indicates the formation of a more ordered activated complex in these cases.

A linear free energy relationship is obtained between the dissociation rate constant,  $k_d^{NiL_2}$ , for the cyanide independent path and  $\beta_2$ , the overall stability constant of the respective complexes, where L is dien, en or Par (Fig. III.6). Table III.8 summarises the equilibrium and rate constant data obtained from these studies.

In summary an attempt has been made at understanding of the exchange reactions of bis chelates of dien and en with nickel(II) and a mechanistic scheme has been proposed to incorporate all the experimental observations. The difference in kinetic behaviour of the two polyamine complexes has been explained on the basis of labilities of water molecules in  $Ni(en)_2$  by virtue of cis and trans locations of these molecules with respects to en ligand in the bis complex.

Table III.8. Summary of the rate constants and equilibrium constants.

	Ni(dien) <sub>2</sub>	Ni(en) <sub>2</sub>	Ni(par) <sub>2</sub> <sup>*</sup>
log K <sub>NiL</sub>	10.7	7.6	17.8
log K <sub>NiL<sub>2</sub></sub> <sup>NiL</sup>	18.9	15.1	22.2
k <sub>d</sub> <sup>NiL</sup> <sub>2</sub> , S <sup>-1</sup>	3.85 x 10 <sup>-2</sup>	5.1	1.86 x 10 <sup>-5</sup> <sup>a</sup>
k <sub>3</sub> , M <sup>-1</sup> S <sup>-1</sup>	1.34 ± 0.14 x 10 <sup>3</sup>	-	1.1 x 10 <sup>-2</sup> <sup>a</sup>
k <sub>CN</sub> <sup>NiL</sup> , M <sup>-1</sup> S <sup>-1</sup>	1.65 x 10 <sup>3</sup>	-	4.45 x 10 <sup>-2</sup>
k <sub>H<sub>2</sub>CN</sub> <sup>NiL</sup> , M <sup>-1</sup> S <sup>-1</sup>	1.25 x 10 <sup>3</sup>	-	4.20 x 10 <sup>-2</sup>
K <sub>4</sub> <sup>-1</sup> k <sub>-3</sub> , S <sup>-1</sup>	4.86 ± 0.1 x 10 <sup>-6</sup>	3.38 ± 0.24 x 10 <sup>-4</sup>	4.4 x 10 <sup>-6</sup> <sup>a</sup>
k <sub>CN</sub> <sup>NiL</sup> <sub>2</sub> , M <sup>-1</sup> S <sup>-1</sup>	6.8 ± 0.7 x 10 <sup>4</sup>	1.3 x 10 <sup>3</sup>	-

\* from Ref. 16

a at pH = 9.0 ± 0.1

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## CHAPTER IV

### KINETICS AND MECHANISM OF FORMATION OF AMINOCARBOXYLATO NICKELATE(II) COMPLEXES FROM (TRIETHYLENETETRAAMINE) NICKEL(II) CHELATE\*

#### ABSTRACT

The kinetics of formation of  $NiL^{2-n}$ , where L is HEEDTA (hydroxyethyl-ethylenediaminetri[acetic acid]) and DTPA (Diethylene triaminepentaacetic acid) from  $Ni(Trien)^{2+}$  (triethylenetetraamine nickel(II)) has been investigated. The order with respect to  $Ni(Trien)$  and aminocarboxylate are found to be one in each reactant. The reaction has been studied at pH 5.5-11.0,  $I=0.1M$  ( $NaClO_4$ ) and followed by the cyanide quenching method. The second order rate constants are estimated by the initial rate method and confirmed by the integrated second order plots. The rate of reaction first decreases with an increase of pH, passes through a minimum at  $pH \approx 8$  and again increases. The behaviour is explained on the basis of reactivities of protonated and hydroxo

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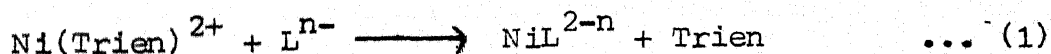
\* published in part in the Ind. J. Chem., 1981, 19(A), 1070-1074.

species of nickel complexes and protonated forms of aminocarboxylates. A reaction mechanism is proposed involving a series of mixed ligand intermediates where steric effects prevent full chelation of the six coordination sites of nickel ion by the two exchanging ligands.

#### IV.1 INTRODUCTION

The mechanisms of nickel polyamine formation and dissociation reactions have been thoroughly studied<sup>1-5</sup>. The dissociation involves the nickel-nitrogen bond breakage followed by nickel solvent bond formation. The rate determining step for the formation reaction is the rate of metal-water loss immediately preceding the first nickel-nitrogen bond formation. The exchange reaction of metal ion takes place via associative and dissociative mechanisms<sup>6</sup>. Ligand exchange reactions involving nickel polyamines with EDTA<sup>7</sup>, HEEDTA, TMDTA<sup>8</sup> and 1,10-phenanthroline<sup>9</sup> have been investigated and shown to proceed through intermediates having both the ligands coordinated to the central metal ion. The reactions are very sensitive to steric effects.

The reaction investigated in this chapter is



where Trien is Triethylene tetraamine and L is HEEDTA (hydroxy ethyl ethylenediamine triacetic acid) and DTPA (diethylenetriaminepentaacetic acid).

## IV.2 EXPERIMENTAL SECTION

All the chemicals used were of AR grade, Triethylene tetraamine (A.R. Fluka) was purified by distillation under reduced pressure. Solutions of Trien were standardised potentiometrically using a pH meter. The preparation and standardisation of  $\text{Ni}(\text{Trien})^{2+}$  complex solutions were carried out by methods previously reported<sup>7,9</sup>. The free acids  $\text{HEEDTAH}_3$  (K & K labs) and  $\text{DTPAH}_5$  (Sigma Chemicals) were recrystallised from ethanol-water mixture and standardised potentiometrically. The ionic strength was maintained at 0.1M with  $\text{NaClO}_4$ . All absorption measurements were made on a Toshniwal Spectrophotometer, model RL-02 (Beckman DU Type) equipped with a thermostated cell compartment. An Elico digital pH meter model LI-120 was used for checking the pH of solutions. The pH was maintained at 11 and 6 by adding NaOH or  $\text{HClO}_4$  for HEEDTA and DTPA reactions respectively except when effect of pH was investigated. The rates of reactions were measured at 267 nm ( $\lambda_{\text{max}}$  of  $\text{Ni}(\text{CN})_4^{2-}$ ) by the cyanide quenching method described earlier<sup>7-8</sup>.

## IV.3 RESULTS

### IV.3.1 Protonation and stability constants and species distributions:

The protonation constants of Trien, HEEDTA and DTPA, and the stability constants of  $\text{Ni}(\text{Trien})^{2+}$ ,  $\text{Ni}(\text{HEEDTA})^{1-}$  and  $\text{Ni}(\text{DTPA})^{3-}$  are listed in Table IV.1. The species distribution of reactants at a particular pH, calculated following Perrin and Sayce<sup>10</sup> from the  $\text{pK}_a$ 's of the complexes and the ligands are shown in Fig.IV.1, IV.2 and IV.3.

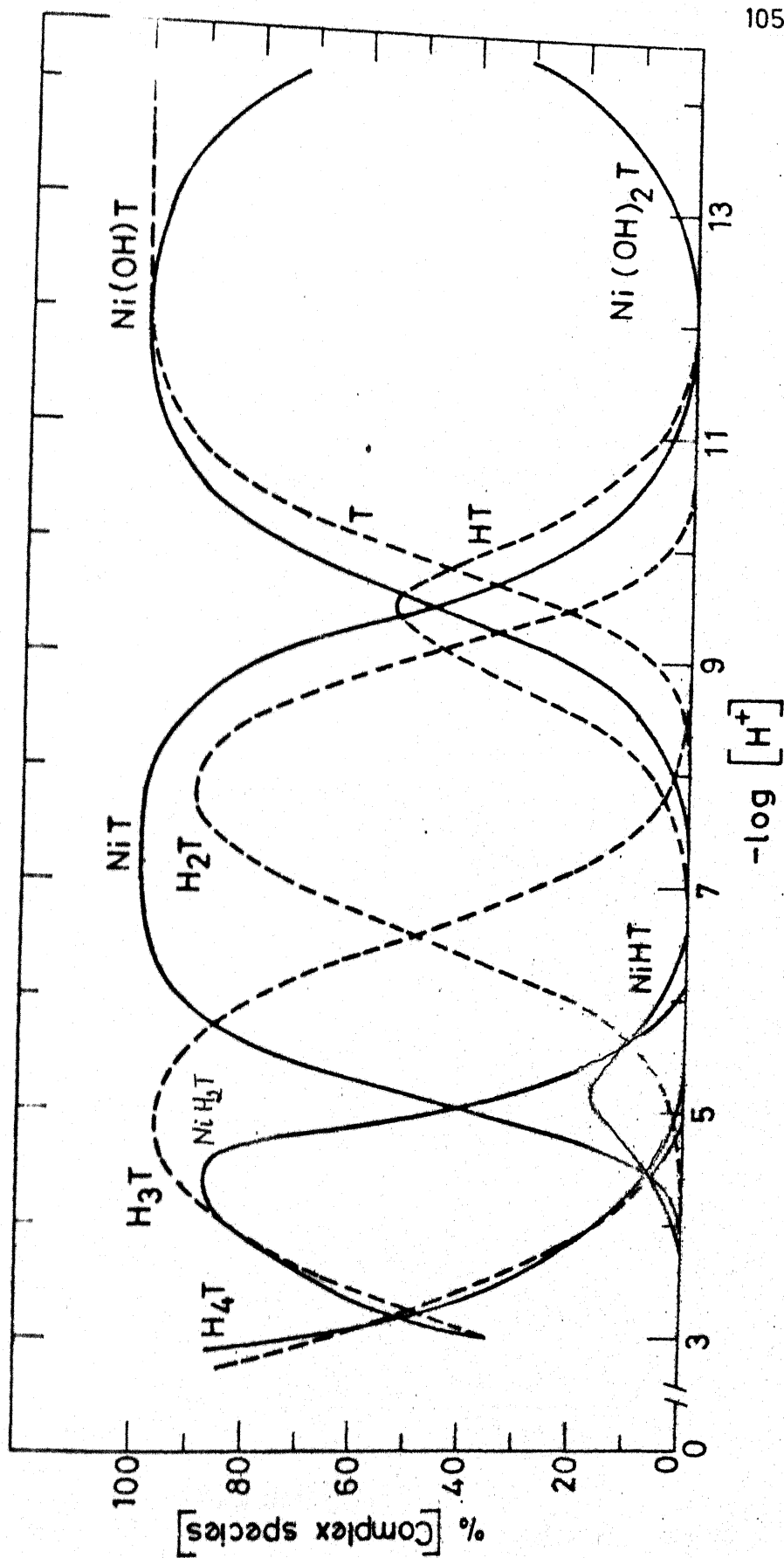


Fig.IV.1 Species distribution of Trien and NiTrien as a function of pH:  $[NiTrien]_T = [Trien]_T = 5.0 \times 10^{-4} M$ .



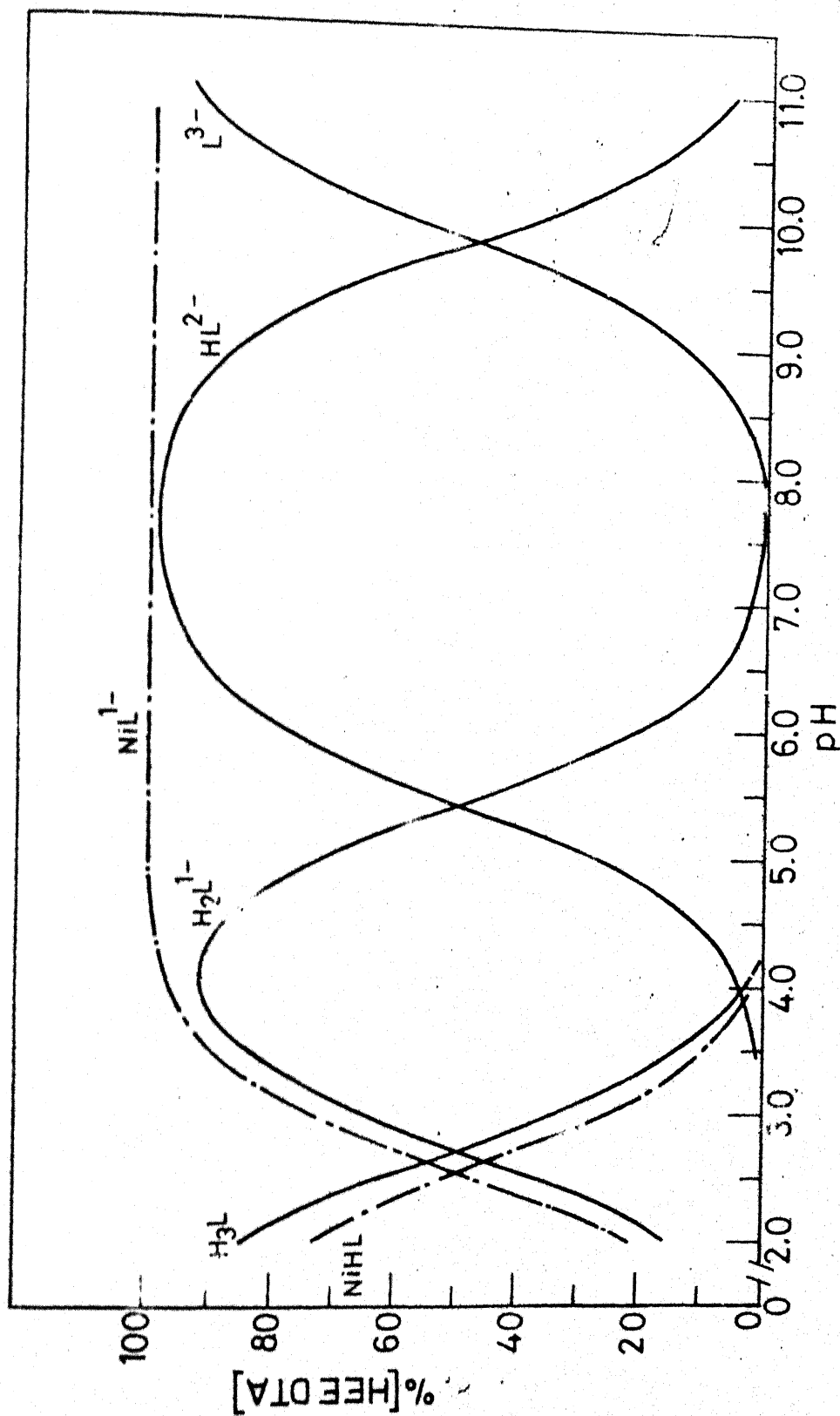


Fig. IV.2 Distribution of protonated and unprotonated forms of HEE DTA and NiHEEDTA complex as a function of pH:  $[NiHEEDTA]_T = [HEEDTA]_T = 5.0 \times 10^{-4} \text{ M}$ .

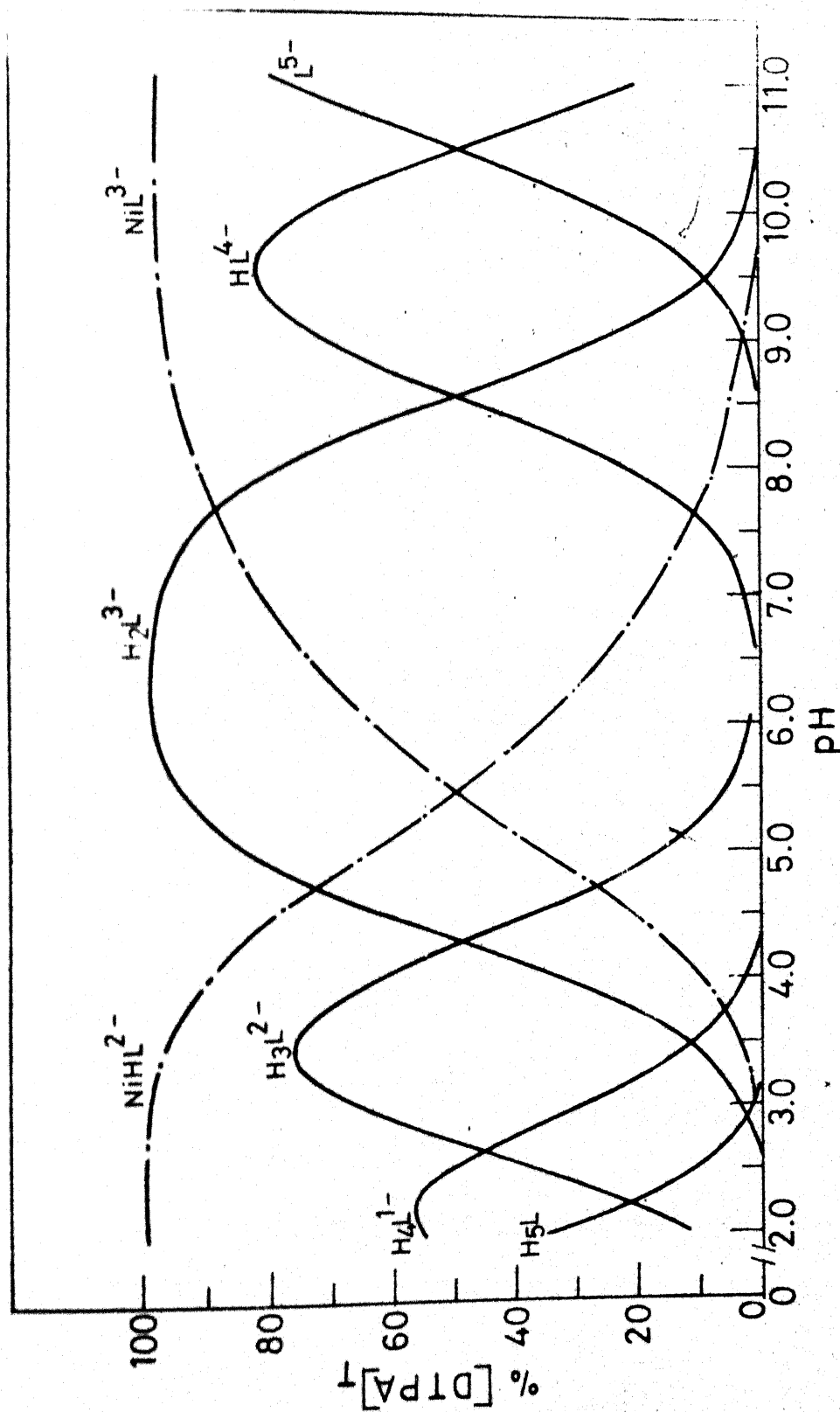


Fig. IV.3 Species distribution of DTPA and NiDTPA as function of pH;  
 $[\text{NiDTPA}]_T = [\text{DTPA}]_T = 5.0 \times 10^{-4} \text{ M}$ .

TABLE IV.1. Protonation Constants of Trien\*, DTPA\*\* and HEEDTA\*\*\* and Formation Constants of their Complexes with Nickel(II) at 25°C.

Protonation constants	TRIEN ( I = 0.1 M)	DTPA ( I = 0.1 M)	HEEDTA ( I = 0.1 M)
$pK_{H_5L}$	-	2.01	-
$pK_{H_4L}$	3.25	2.41	-
$pK_{H_3L}$	6.25	4.26	2.72
$pK_{H_2L}$	9.08	8.60	5.41
$pK_{HL}$	9.88	10.55	9.81
<u>Stability constants</u>			
$\log K_{NiL}^{Ni}$	13.82	20.17	17.10
$\log K_{NiHL}^{Ni}$	8.70	-	-
$\log K_{NiHL}^{NiL}$	4.70	5.67	2.54 <sup>a</sup>
$\log K_{NiL(OH)}^{NiL}$	4.50	-	-

\*\* DTPA is diethylenetriamine pentaacetic acid.

\* TRIEN is triethylenetetramine.

\*\*\* HEEDTA is (hydroxy ethyl)ethylenediamine tri acetic acid.

a I = 1.25 M.

### IV.3.2 Reaction of aminocarboxylates with Ni(Trien)<sup>2+</sup>

The reactions of aminocarboxylates viz. DTPA and HEEDTA with Ni(Trien) were studied at pH 5.0-11.0. The reaction orders were obtained from the slopes of initial rate plots determined by the plane mirror method<sup>11</sup>. The reaction was found to be first order each with respect to aminocarboxylate and nickel polyamine complex (Table IV.2, Fig. IV.4) respectively which is in

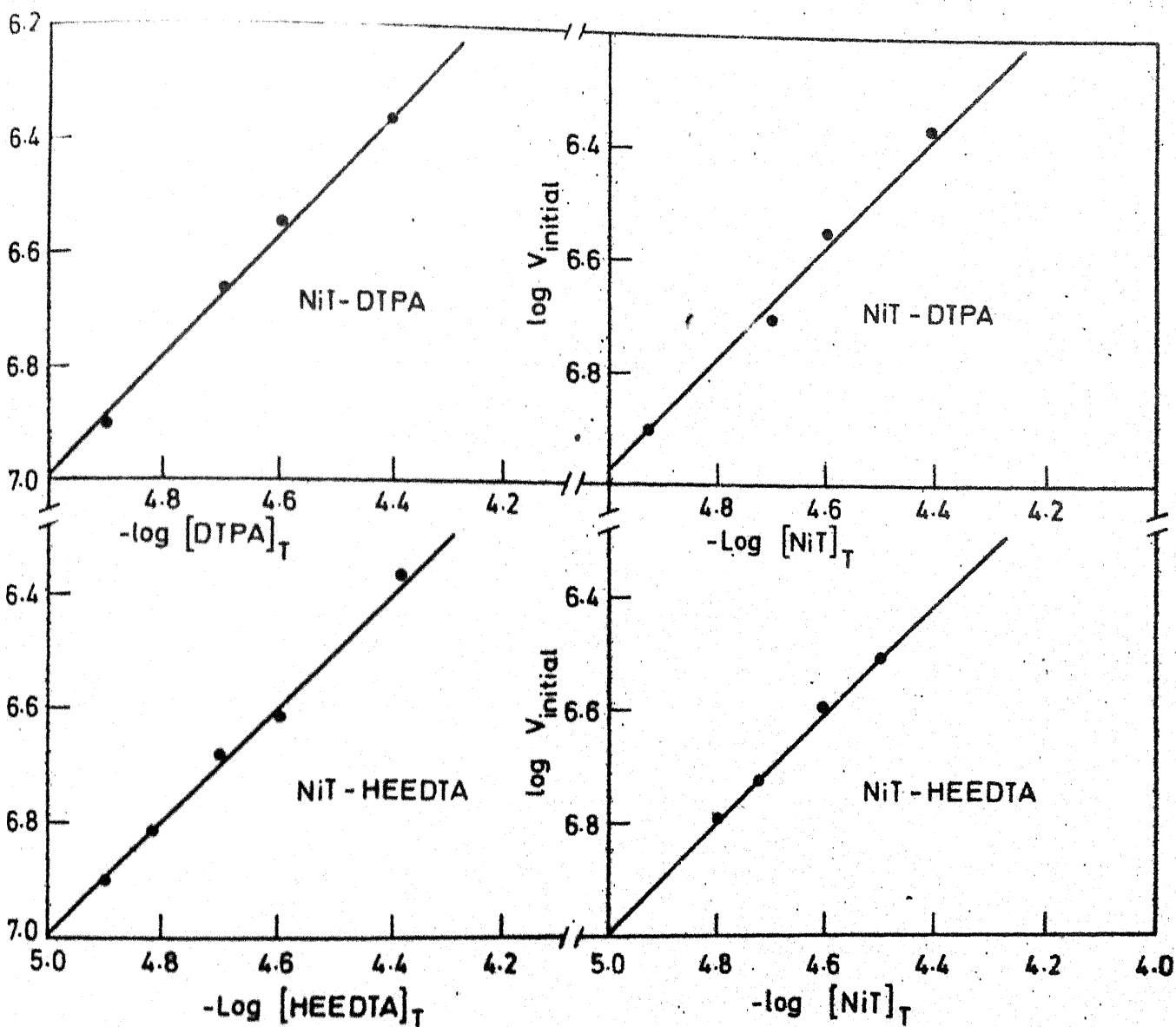
Table IV.2. Dependence of Initial Rates on the Concentration of Reactants.

#### A. NiTrien-HEEDTA System

Temp. =  $25 \pm 0.1^\circ\text{C}$ ; pH =  $11.0 \pm 0.05$  and I = 0.1M (NaClO<sub>4</sub>)

$[\text{NiTrien}^{+2}]_T$ $\times 10^5, \text{M}$	$10^5 \times [\text{HEEDTA}]_T, \text{M}$	$10^7 \times \text{Initial rate,}$ $(V_1), \text{M} \cdot \text{s}^{-1}$	$10^{-2} \times k_{LT}^{\text{NiT}}$
2.50	4.00	4.25	4.01
2.50	2.50	2.44	3.90
2.50	2.00	2.05	4.10
2.50	1.50	1.54	4.11
2.50	1.25	1.25	4.10
2.00	2.50	2.07	4.14
1.50	2.50	1.50	4.00
1.25	2.50	1.32	4.22

$$\text{Av. } k_{LT}^{\text{NiT}} = 4.05 \pm 0.1 \times 10^2 \text{ M}^{-1}\text{S}^{-1}$$



V.4 Order dependence in aminocarboxylates and polyamine complex for the reaction of  $\text{NiTrien}^{2+}$  with aminocarboxylates.

B. NiTrien-DTPA System

Temp. =  $25 \pm 0.1^\circ\text{C}$ ; pH = 6.0; I = 0.1M ( $\text{NaClO}_4$ )

$[\text{NiTrien}^{+2}]_T \times 10^5, \text{M}$	$[\text{DTPA}]_T \times 10^5, \text{M}$	Initial Rate $\times 10^7, \text{MS}^{-1}$	$k_{LT}^{\text{NiT}} \times 10^{-2}, \text{M}^{-1}$
4.00	4.00	6.96	4.35
2.50	2.50	2.84	4.54
2.50	1.25	1.41	4.52
2.50	2.00	2.20	4.40
2.50	4.00	4.38	4.38
3.87	2.50	4.41	4.56
1.95	2.50	2.21	4.54
1.15	2.50	1.29	4.46
Av. $k_{LT}^{\text{NiT}} = (4.48 \pm 0.09) \times 10^2 \text{ M}^{-1}\text{S}^{-1}$			

accordance with the rate law given in Equation (2).

$$\frac{-d[\text{NiT}]_T}{dt} = k_{LT}^{\text{NiT}} [\text{NiT}]_T [\text{L}]_T \quad \dots (2)$$

where  $[\text{NiT}]_T$  and  $[\text{L}]_T$  represent the total concentration of protonated and unprotonated forms of  $\text{Ni}(\text{Trien})^{2+}$  and amino-carboxylates respectively and  $k_{LT}^{\text{NiT}}$  is the observed second order rate constant for these two reactions. The values of  $k_{LT}^{\text{NiT}}$ , calculated by the initial rate method were checked with those obtained from integrated rate plots. The second order rate plots

were linear over more than 60% of the reaction and extrapolated through the theoretical intercept. A slight deviation for the later points is due to contribution from the reverse reaction.

#### IV.3.3 Effect of Temperature on the reaction rate:

Both reactions were carried out in a range of temperature from 20°-40°C and 25°-40°C respectively. The activation parameters were evaluated using Arrhenius plots ( $\log k_{LT}^{NiT}$  vs  $\frac{1}{T}$ ) and are given in Table IV.3. The low enthalpies of activation

Table IV.3. A. Effect of Temperature on the Reaction of HEEDTA with  $Ni(Trien)^{+2}$ .

$$[NiTrien]_T^{2+} = [HEEDTA]_T = 2.50 \times 10^{-5} M$$

$$pH = 11.0 \pm 0.01; I = 0.1M (NaClO_4)$$

Temp. $\pm 0.1^\circ C$	$10^{-2} \times k_{LT}^{NiT}$ , $M^{-1}S^{-1}$	Kinetic Parameters, $mol^{-1}$
25	4.33	$E_a, Kcal = 3.6$
30	4.65	$\Delta H^\ddagger, kcal = 3.0$
35	5.29	$\Delta S^\ddagger, e.u. = -36$
40	5.75	$pZ, cm^{-1} = 7.1 \times 10^4$

B. Effect of Temperature on the exchange of DTPA with NiTrien

$$[\text{NiTrien}^{2+}]_T = [\text{DTPA}]_T = 2.50 \times 10^{-5} \text{M};$$

$$\text{pH} = 6.0 \text{ and } I = 0.1 \text{M (NaClO}_4\text{)}$$

Temp. $\pm 0.1^\circ\text{C}$	$k_{LT}^{\text{NiT}} \times 10^{-2},$ $\text{M}^{-1}\text{S}^{-1}$	Kinetic Parameters, $\text{mole}^{-1}$
20	3.72	$E_a, \text{kcal} = 5.2$
25	4.38	$\Delta H^\ddagger, \text{kcal} = 4.6$
30	5.16	$\Delta S^\ddagger, \text{e.u.} = -30.8$
35	5.85	$p_z, \text{cm}^{-1} = 1.1 \times 10^6$
40	6.70	

indicate an associative mechanism where bond breaking and making takes place simultaneously. The negative entropy of activation suggests steric blocking and a highly ordered reaction pathway.

#### IV.3.4 Effect of hydrogen ion concentration on reaction rates:

It was found that the reaction rate constants are strongly dependent on the hydrogen ion concentration in the pH range 5-11. (Table IV.4). This may be attributed to the reactivities of various protonated, unprotonated and hydroxo forms of the reactants. On the basis of known protonation constants of



Table IV.4. A. Effect of pH on the Rate of Exchange of HEEDTA with NiTrien

$$[\text{NiTrien}^{2+}]_T = [\text{HEEDTA}]_T = 2.50 \times 10^{-5} \text{M}$$

$$\text{Temp.} = 25 \pm 0.1^\circ\text{C}; I = 0.1\text{M} (\text{NaClO}_4)$$

pH	$10^{-2} \times k_{LT}^{\text{NiT}} \text{ M}^{-1}\text{S}^{-1}$	pH	$10^{-2} \times k_{LT}^{\text{NiT}} \text{ M}^{-1}\text{S}^{-1}$
5.5	9.97	8.5	2.25
6.0	5.76	9.0	3.16
6.5	4.02	9.5	3.57
7.0	3.31	10.0	3.27
7.5	3.03	10.5	3.64
8.0	2.09	11.0	4.33

B. Effect of pH on the Rate of Exchange of DTPA with Nickel Trien

$$[\text{NiTrien}^{2+}]_T = [\text{DTPA}]_T = 2.5 \times 10^{-5} \text{M};$$

$$\text{Temp.} = 25 \pm 0.1^\circ\text{C}; I = 0.1\text{M} (\text{NaClO}_4)$$

pH	$k_{LT}^{\text{NiT}} \times 10^{-2} \text{ M}^{-1}\text{S}^{-1}$	pH	$k_{LT}^{\text{NiT}} \times 10^{-2} \text{ M}^{-1}\text{S}^{-1}$
5.2	11.10	8.3	2.81
5.6	7.34	8.6	2.98
5.8	5.58	8.9	3.76
5.9	5.10	9.4	4.29
6.0	4.48	9.7	4.89
6.7	4.18	10.0	4.11

...contd.

7.0	3.50	10.1	4.35
7.3	3.16	10.45	4.36
7.5	2.83	11.0	4.32
8.0	2.70		

---

amino carboxylates and  $\text{Ni}(\text{Trien})^{2+}$ , the following rate equation (3) is proposed for the reaction of HEEDTA with  $\text{Ni}(\text{Trien})^{2+}$ .

$$\text{Rate} = \{ k_L^{\text{NiTOH}} [\text{OH}^-] [\text{L}^{n-}] + k_L [\text{L}^{n-}] + k_{\text{HL}} [\text{HL}^{1-n}] + k_{\text{H}_2\text{L}} [\text{H}_2\text{L}^{2-n}] \} \cdot [\text{NiT}^{2+}] \quad \dots (3)$$

in the pH range below 8, first two terms which do not involve protons can be ignored and under this condition equation (3) transforms to equation (4) or (5)

$$\text{Rate} = \{ k_{\text{HL}} K_1 [\text{H}^+] + k_{\text{H}_2\text{L}} K_1 K_2 [\text{H}^+]^2 \} [\text{NiT}^{2+}] [\text{L}^{n-}] \dots (4)$$

where  $K_1$  &  $K_2$  are the first and second protonation constants of HEEDTA. In Equation (5)  $k_1$  &  $k_2$  are the composite rate constants and are equal to  $k_{\text{HL}} \cdot K_1$  and  $k_{\text{H}_2\text{L}} \cdot K_1 K_2$  respectively.

$$\text{Rate} = \{ k_1 [\text{H}^+] + k_2 [\text{H}^+]^2 \} [\text{NiT}^{2+}] [\text{L}^{n-}] \quad \dots (5)$$

Comparing equations (5) and (2) we get

$$k_{\text{LT}}^{\text{NiT}} \frac{[\text{NiT}]_T}{[\text{NiT}^{2+}]} \cdot \frac{[\text{L}]_T}{[\text{L}^{n-}]} = k_1 [\text{H}^+] + k_2 [\text{H}^+]^2 \quad \dots (6)$$

where  $\frac{[L]_T}{[L^{n-}]} = 1 + K_1[H^+] + K_1K_2[H^+]^2 + K_1K_2K_3[H^+]^3$ ;  
 $K_1, K_2$  and  $K_3$  being the three protonation constants of HEEDTA.  
 Also,

$$\frac{[NiT]_T}{[NiT^{2+}]} = 1 + K_{NiHT}^{NiT} [H^+] + K_{NiT(OH)}^{NiT} [OH^-] + K_{NiT(OH)_2}^{NiT} [OH^-]^2$$

Equation (6) can be rewritten as

$$K_{LT}^{NiT} \frac{[NiT]_T}{[NiT^{2+}]} \frac{[L]_T}{[L^{3-}]} \frac{1}{[H^+]} = k_1 + k_2 [H^+] \quad \dots (7)$$

The plot of left hand side of Eqn. (7) vs  $[H^+]$  gives a straight line (Fig. IV.5x) with an intercept  $k_1 = K_{HL}^{NiT} K_1 = 1.5 \times 10^{12}$

or  $K_{HL}^{NiT} = \frac{1.5 \times 10^{12}}{K_1} = 2.37 \times 10^2 \text{ M}^{-2} \text{ S}^{-1}$

Also, slope  $= K_{H_2L}^{NiT} K_1 K_2 = 3.25 \times 10^{18}$  or

$$K_{H_2L}^{NiT} = \frac{3.25 \times 10^{18}}{K_1 \cdot K_2} = 2.2 \times 10^3 \text{ sec}^{-1}$$

Above pH 8.5 the other two terms can be evaluated from the data at higher pH value by correcting for the contribution of  $K_{HL}$  and  $K_{H_2L}$  employing equation (8)

$$A - \{ k_1 [H^+] + k_2 [H^+]^2 \} = K_L^{NiT} + K_L^{NiT(OH)} K_{NiT(OH)}^{NiT} [OH^-] \dots (8)$$

where A represents  $[H^+]$  times the left hand side of equation 7. On replacing  $[OH^-]$  by  $K_w / [H^+]$ , equation (8) is transformed to equation (9)

$$A - \{ k_1 [H^+] + k_2 [H^+]^2 \} = K_L^{NiT} + K_L^{NiT(OH)} K_{NiT(OH)}^{NiT} \frac{K_w}{[H^+]} \dots (9)$$

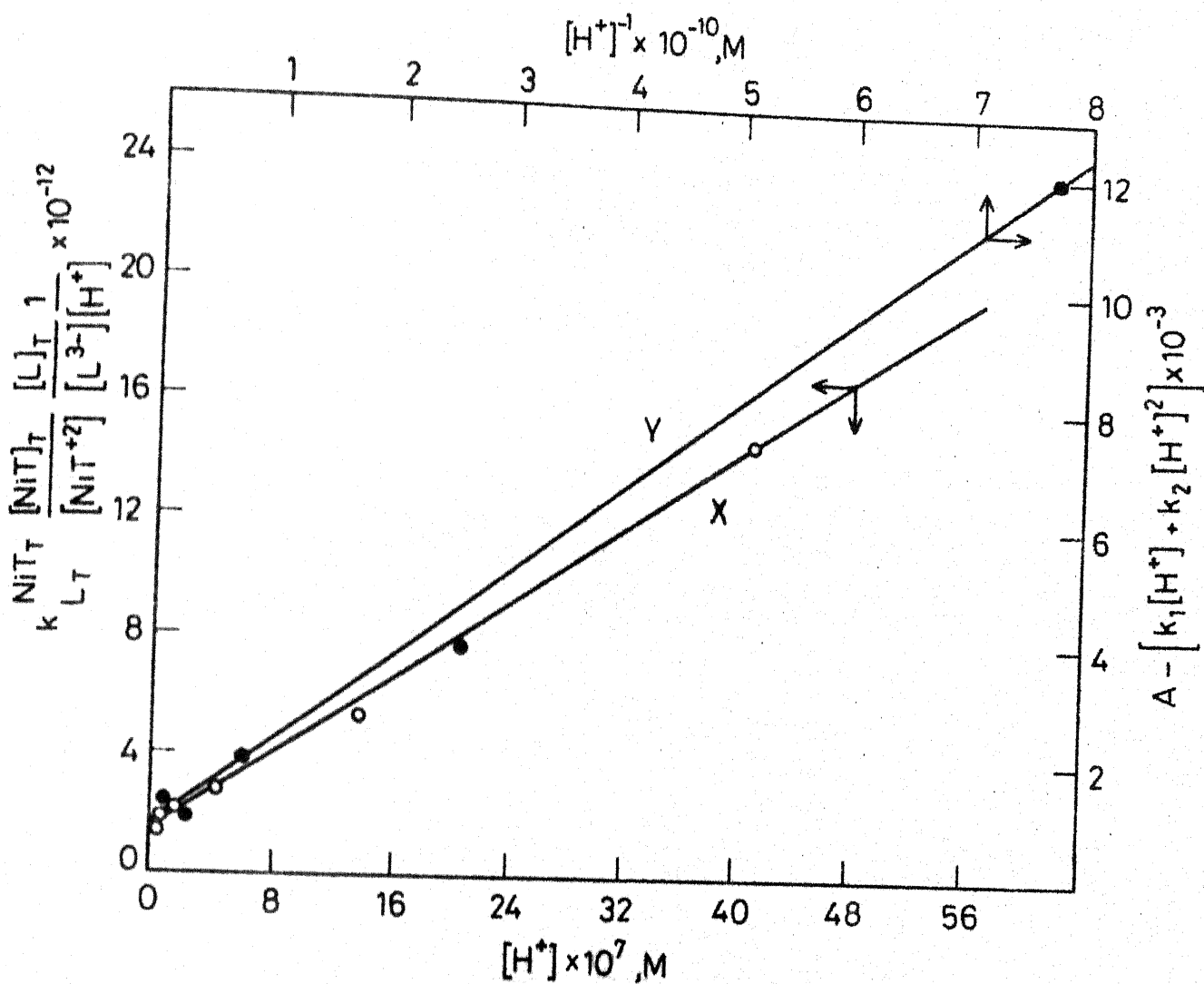


Fig. IV.5 Resolution of the rate constants for the reaction of NiTrien<sup>2+</sup> with HEEDTA. temp.=25°C and I=0.1M. 'X', Plot of eq.(7) and 'Y', Plot of eq.(9).

So, a plot of left hand side of equation (9) vs  $\frac{1}{[H^+]}$  gives a straight line (Fig. IV.5y) with an intercept  $-k_L^{NiT} = 8.0 \times 10^2 M^{-1} s^{-1}$  and slope  $= k_L^{NiT(OH)} \frac{k_{NiT}^{NiT}}{K_{NiT(OH)} K_W} = 1.44 \times 10^{-7} sec^{-1}$

$$\text{or } k_L^{NiT(OH)} = 4.56 \times 10^2 M^{-2} s^{-1}$$

Similarly for the reaction of DTPA with NiTrien the following rate equation is proposed.

$$\begin{aligned} \text{rate} = & \{ k_L^{NiT(OH)} [OH^-] [L^{n-}] + k_L [L^{n-}] + k_{HL} [HL^{1-n}] + k_{H_2L} [H_2L^{2-n}] \\ & + k_{H_3L} [H_3L^{3-n}] \} [NiT^{2+}] \quad \dots (10) \end{aligned}$$

Using the protonation constants of DTPA and hydroxo constants of Ni Trien, at different pH ranges, the following three equations (11, 12 and 13) can be obtained by an algebraic manipulation similar to the one for HEEDTA reaction as outlined above.

In pH range 5.5 - 6.5

$$k_L^{NiT} \frac{[NiT]_T}{[NiT^{2+}]} \frac{[L]_T}{[L^{5-}]} \frac{1}{[H^+]^2} = k_2 + k_3 [H^+] \quad \dots (11)$$

and in pH range 6.5 - 9

$$A [H^+]^2 - \{ k_2 [H^+]^2 + k_3 [H^+]^3 \} = k_1 [H^+] \quad \dots (12)$$

and lastly above pH 9

$$D - k_1 [H^+] = k_L^{NiT} + k_L^{NiT(OH)} \frac{k_{NiT}^{NiT}}{K_{NiT(OH)} K_W} \frac{1}{[H^+]} \quad \dots (13)$$

where  $k_1$ ,  $k_2$  and  $k_3$  are composite rate constants and are equal to  $k_{HL}K_1$ ,  $k_{H_2L}K_1K_2$  and  $k_{H_3L}K_1K_2K_3$  respectively;  $K_1$ ,  $K_2$  and  $K_3$  being the first three protonation constants of DTPA. 'A' represents left hand side of equation (11) and 'D', the left hand side of equation (12). The various rate constants can be resolved using the above three equations. For example, by plotting left hand side of equation (11) vs  $[H^+]$  (Fig. IV.6x) we get  $k_{H_2L}$  and  $k_{H_3L}$ ; by plotting left hand side of equation (12) vs  $[H^+]$  (Fig. IV.6y) we get  $k_{HL}$  and from the plot of left hand side of equation (13) vs  $\frac{1}{[H^+]}$  (Fig. IV.6z) we get  $k_L$  and  $k_L^{NiT(OH)}$ .

The various resolved rate constants for both systems are given in Table IV.5. The observed pH dependence of rate for the

Table IV.5. Evaluated Rate Constants<sup>a</sup> with Alternate Assignment of Protons at 25°C and I = 0.1M (NaClO<sub>4</sub>).

A. NiTrien + HEEDTA System

$$k_L^{Ni(OH)T} = 4.56 \times 10^2$$

$$k_L^{NiT} = 8.0 \times 10^2$$

$$k_{HL}^{NiT} = 2.37 \times 10^2$$

$$k_{H_2L}^{NiT} = 2.2 \times 10^3$$

$$k_L^{NiHT} = 3.19 \times 10^7$$

$$k_{HL}^{NiHT} = 1.18 \times 10^4$$

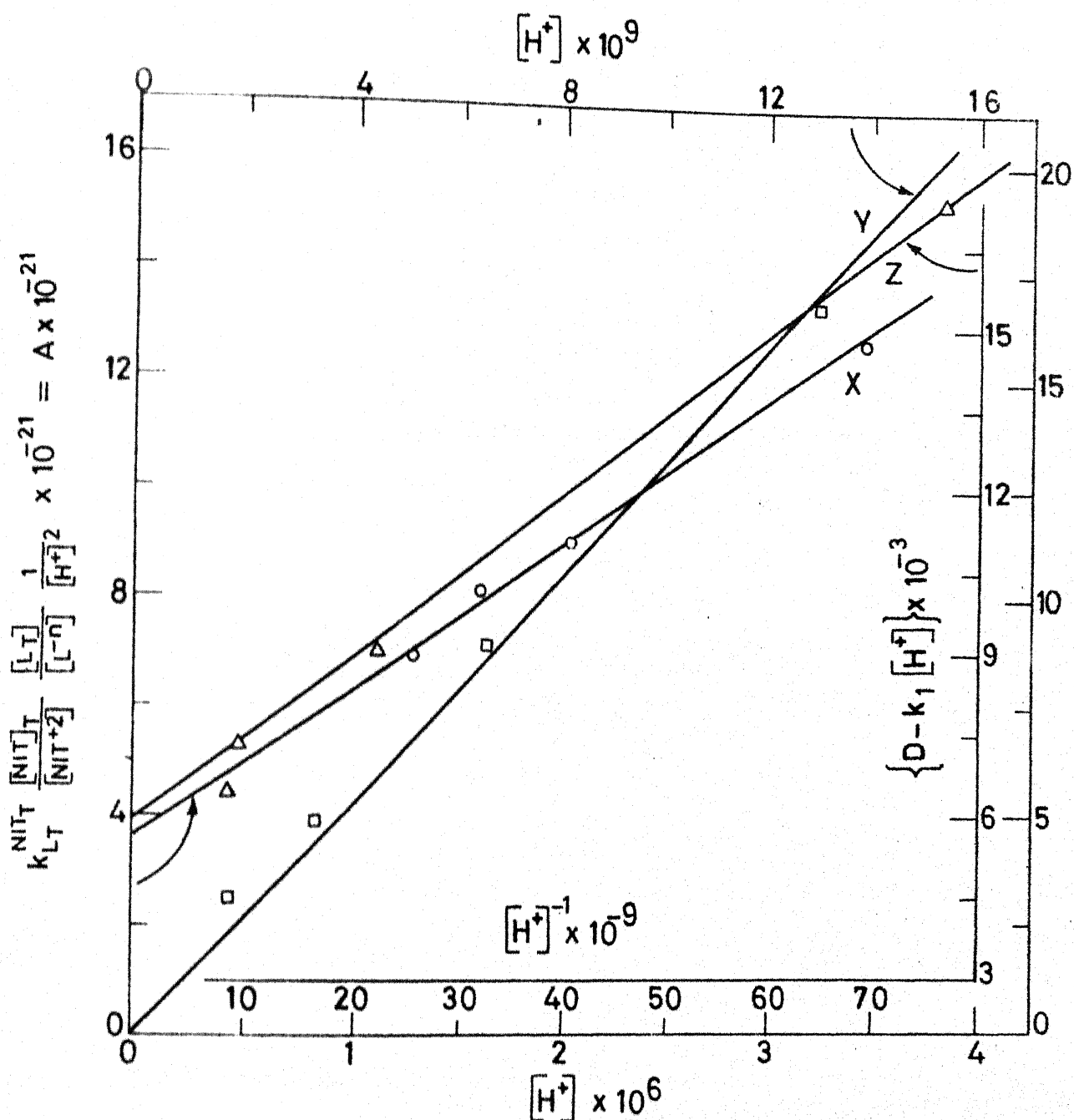


Fig. IV.6 Resolution of rate constants viz.  $k_{\text{H}_3\text{L}}^{\text{NiT}}$ ,  $k_{\text{H}_2\text{L}}^{\text{NiT}}$ ,  $k_{\text{HL}}^{\text{NiT}}$ ,  $k_{\text{L}}^{\text{NiT}}$  and  $k_{\text{L}}^{\text{Ni(OH)T}}$  for the reaction of  $\text{NiTrien}^{2+}$  with DTPA. temp. =  $25^\circ\text{C}$  and  $I=0.1\text{M}$ . 'X', Plot of eq.(11), 'Y', Plot of eq.(12) and 'Z', Plot of eq.(13).

### B. NiTrien-DTPA System

$$k_L^{Ni(OH)T} = 4.65 \times 10^2$$

$$k_L^{NiT} = 6.0 \times 10^3$$

$$k_{HL}^{NiT} = 3.52 \times 10^2$$

$$k_{H_2L}^{NiT} = 2.55 \times 10^2$$

$$k_{H_3L}^{NiT} = 1.05 \times 10^4$$

$$k_L^{NiHT} = 2.61 \times 10^8$$

$$k_{HL}^{NiHT} = 2.12 \times 10^6$$

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a. Units given in text.

reaction is shown in Fig. IV.7 for HEEDTA and Fig. IV.8 for DTPA. The solid line is calculated from the resolved rate constants and relevant  $pK'_a$ 's. The agreement between theoretical curve and experimental points is reasonably good.

### IV.4 DISCUSSION

It has been reported that the rate of dissociation of nickel polyamine complexes<sup>4</sup> is much slower to account for the exchange rate of these complexes with multidentate ligands like aminocarboxylates. Therefore, the presence of aminocarboxylates in solutions appears to facilitate the dissociation of Ni(Trien). Presumably the exchange process takes place through a succession of bond formation and bond rupture steps.

Since the stabilities of nickel complexes of polyamines and polyaminocarboxylate ligands increase as the number of dentates increases (upto maximum no. of six) nickel(II) in each



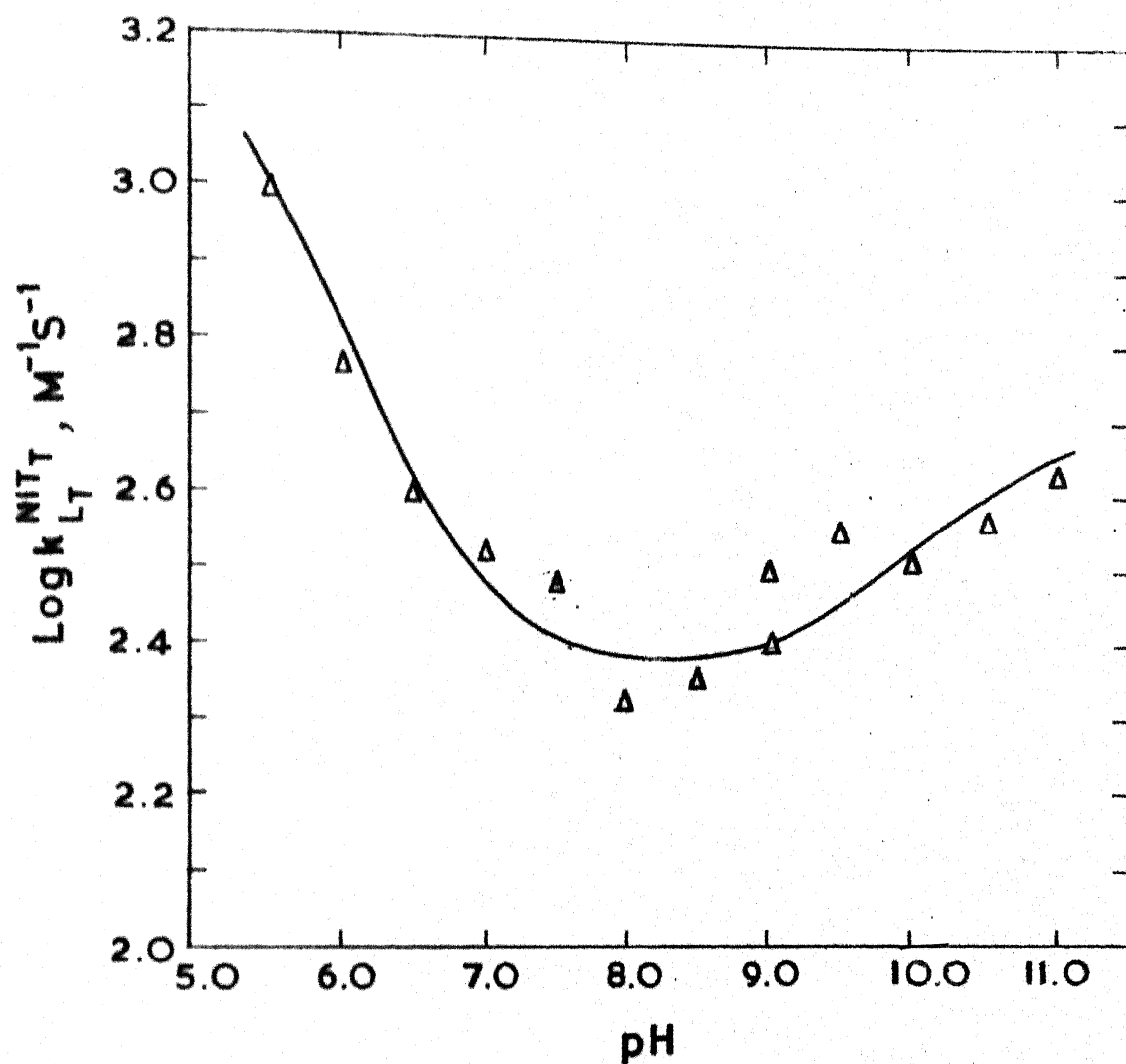


Fig. IV.7 Fit of theoretical curve to the observed rate constants for HEEDTA exchange with NiTrien. temp. = 25°C and  $I = 0.1\text{M}$ .

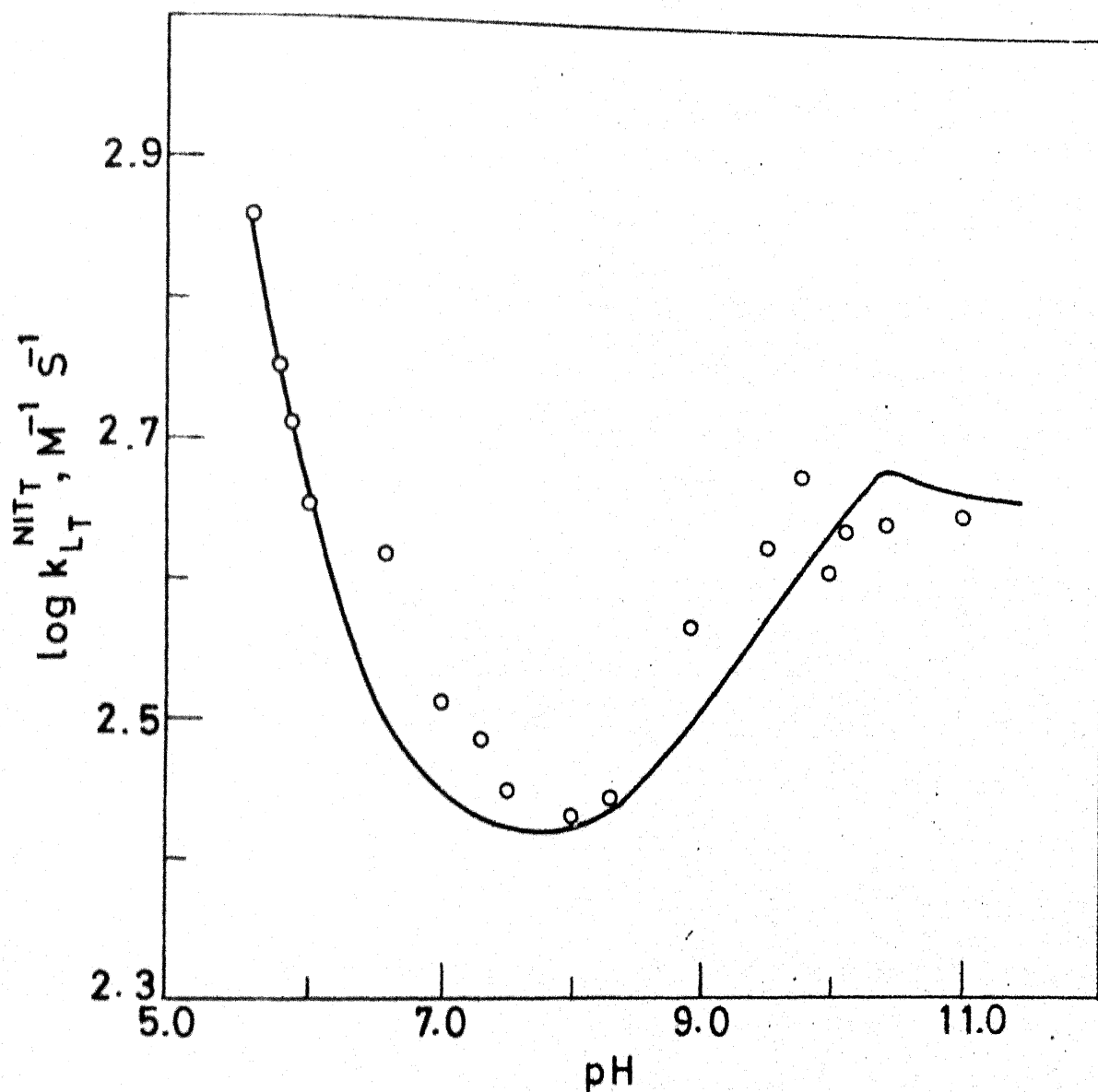


Fig. IV.8 Fit of theoretical curve to the experimentally observed rate constants for the reaction of NiTrien with DTPA. temp.  $\approx 25^{\circ}C$  and  $I = 0.1M$ .

intermediate species should form as many coordination bonds to the two multidentate ligands as steric effects will permit. A number of mixed ligand intermediate species may occur in the exchange reaction with successive intermediates exhibiting more coordinate bonds to the incoming ligand and fewer to out going one.

Structural models show that in forming the first bond between the nickel ion (which is initially coordinated with polyamine) and an amino-carboxylate ion, a carboxylate donor group is highly favoured over a nitrogen due to steric configuration of the aminocarboxylate ion and the hindered access of nitrogen atom to the nickel coordination sites. This preference is enhanced by the electrostatic attraction between the carboxylate group and the nickel ion. When one considers the formation of second and subsequent bonds, the factors like steric difficulties and rotational barriers to be encountered for approaching the coordination sites on nickel exclude the possibility that an aminocarboxylate atom can approach the nickel at the same time as the nickel polyamine bond is broken. On the other hand the solvent molecules, in this case water, can rapidly coordinate at this site vacated by a polyamine segment. It is, therefore, proposed as suggested earlier<sup>7,8</sup>, that the mechanism of displacement of a polyamine by an aminocarboxylate molecule consists of two alternating steps: cleavage of a nickel-polyamine bond attended by rapid coordination by water molecules at the vacated site followed by rupture of the nickel-water bond and rapid coordinat

of an aminocarboxylate donor atom, which must rotate to assume a position favourable for bonding. These features of the mechanism proposed above are presented for HEEDTA reaction in Fig. IV.9. The scheme for DTPA reaction will be similar. Here the reaction of only non-protonated reactants has been shown for the sake of clarity. Similar steps were considered in earlier reported reaction of Ni(Trien) with EDTA<sup>7</sup> and Ni(Tetren) with HEEDTA<sup>8</sup>.

The pinpointing of the rate determining step poses a difficult problem, but this should be one of the following processes (a) loss of water<sup>12</sup> or (b) rupture of metal-polyamine bond. It should thus depend upon either the rate constant for water loss (similar to metal-chelate formation) or the rate constant for rupture of the nickel-polyamine bond (similar to metal chelate dissociation).

The observed rate constant of such a reaction is related<sup>7</sup> to rate constant of the rate determining step and the stability constant of the intermediate preceding the rate determining step as in equation (14).

$$k_{\text{expt}} = \frac{K_{(\text{n}^{\text{th}} \text{ intermediate})}}{K_{\text{reactants}}} \cdot k_n \quad \dots (14)$$

where  $K_{(\text{n}^{\text{th}} \text{ intermediate})} =$

$$\frac{K_{\text{polyamine segment}} \cdot K_{\text{aminocarboxylate segment}}}{K_{\text{electrostatic}}}$$

and  $k_n$  is the rate constant for nickel-nitrogen or nickel-water bond breaking process. This has been estimated<sup>4-7</sup> to be close

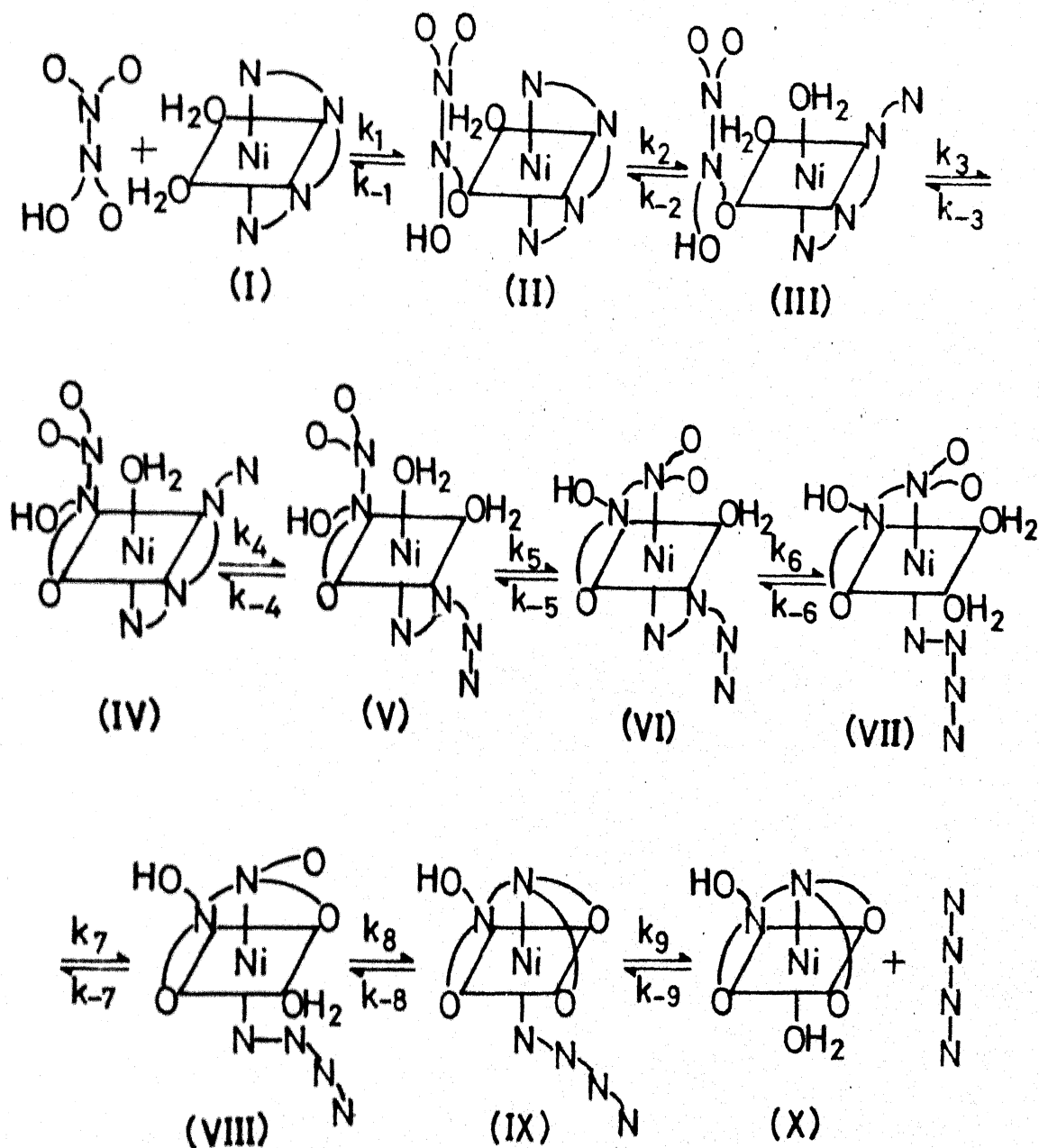


Fig.IV.9 Proposed mechanism for AminoCarboxylate (HEE DTA) exchange reaction with NiTrien.

to  $80 \text{ sec}^{-1}$  for steps involving  $k_2$ ,  $k_4$ ,  $k_6$  and  $k_9$  where rupture of nickel-nitrogen bond takes place.

A value of  $60 \times 10^2 \text{ sec}^{-1}$  has been estimated<sup>4</sup> for steps  $k_5$ ,  $k_7$ ,  $k_8$  etc while for steps  $k_3$  and  $k_5$  where rupture of nickel-aquo bond and formation of nickel-nitrogen bond takes place, it is approximately  $1 \times 10^4 \text{ sec}^{-1}$ .  $K_{\text{electrostatic}}$  is taken to be  $0.1^7$ . As an illustration, the procedure for predicting the rate constant for step 3 is outlined below. For this step,

$$K_{\text{polyamine segment}} = K_{\text{Ni}}^{\text{Ni(dien)}} = 10^{10.7},$$

$$K_{\text{aminocarboxylate segment}} = K_{\text{Ni}}^{\text{Ni(OAc)}} = 10^{0.7},$$

$$K_{\text{electrostatic}} = 0.1; K_{\text{reactant}} = 10^{13.82}$$

$$k_n = 10^4 \text{ sec}^{-1}$$

Inserting these values in Eq. (14) we get

$$k_{\text{expt.}} = \frac{10^{10.7} \times 10^{0.7}}{0.1} \times \frac{10^4}{10^{13.82}} = 3.8 \times 10^2 \text{ M}^{-1} \text{ S}^{-1}$$

The values of  $k_{\text{expt.}}$  have been obtained from equation (14) by a similar procedure for each of the nine steps proposed in the mechanistic scheme given in Fig. IV.9 and these are listed in Table IV.6. The calculated values for DTPA reaction will be same and hence are not separately given.

Table IV.6. Values of predicted rate constants

$$(k_L^{NiT} = \frac{K_{nth}^{intermediate} \cdot k_n}{K_{reactant}}) \text{ for possible rate determining step.}$$

Temp = 25°C;  $K_{electrostatic} = 10^{-1}$ ;  $K_{reactant} = 10^{13.82}$ ;  
 $k_n = 1 \times 10^4$  for steps 3,5; 80 for steps 2,4,6 etc.  
 and  $6 \times 10^2$  for steps 7,8 etc.

From structure	To structure	$K_{nth}^{intermediate} = \frac{K_{polyamine} \cdot K_{aminocarboxylate}}{K_{electrostatic}}$	$k_L^{NiT}, M^{-1}s^{-1}$ (predicted)
II	III	$3.3 \times 10^{15}$	$4.0 \times 10$
III	IV	$2.5 \times 10^{12}$	$3.8 \times 10$
IV	V	$9.8 \times 10^{16}$	$1.1 \times 10$
V	VI	$7.8 \times 10^{13}$	$1.2 \times 10$
VI	VII	$1.1 \times 10^{19}$	$1.3 \times 10$
VII	VIII	$1.7 \times 10^{14}$	$1.5 \times 10$
VIII	IX	$2.7 \times 10^{17}$	$2.4 \times 10$
IX	X	$3.3 \times 10^{21}$	$3.8 \times 10$

$$\begin{aligned}
 * K_{II} &= K_{Ni}^{NiTrien} \cdot K_{Ni}^{NiOAC} / K_{es} = 10^{13.82} \cdot 10^{0.7} \cdot 10^{+1}; \\
 K_{III} &= K_{Ni}^{NiDien} \cdot K_{Ni}^{NiOAC} / K_{es} = 10^{10.7} \cdot 10^{0.7} \cdot 10^{+1}; \\
 K_{IV} &= K_{Ni}^{NiDien} \cdot K_{Ni}^{NiGly} / K_{es} = 10^{10.7} \cdot 10^{5.29} \cdot 10^{+1}; \\
 K_V &= K_{Ni}^{NiNien} \cdot K_{Ni}^{NiGly} / K_{es} = 10^{7.6} \cdot 10^{5.29} \cdot 10^{+1}; \\
 K_{VI} &= K_{Ni}^{NiNien} \cdot K_{Ni}^{NiEDMA} / K_{es} = 10^{7.6} \cdot 10^{10.44} \cdot 10^{+1}; \\
 K_{VII} &= K_{Ni}^{NiNH_3} \cdot K_{Ni}^{NiEDMA} / K_{es} = 10^{2.79} \cdot 10^{10.44} \cdot 10^{+1};
 \end{aligned}$$

...contd.

$$K_{VIII} = K_{Ni}^{NiNH_3} \cdot K_{Ni}^{NiEDDA} / K_{es} = 10^{2.79} \cdot 10^{13.65} \cdot 10^{+1};$$

$$K_{IX} = K_{Ni}^{NiNH_3} \cdot K_{Ni}^{NiHEEDTA} / K_{es} = 10^{2.79} \cdot 10^{17.10} \cdot 10^{+1}.$$

(All stability constants taken from ref. 13)

Trien = triethylenetetramine; Dien = diethylenetriamine;

Gly = glycine; en = ethylenediamine; EDDA = ethylenediaminediacetic acid; OAc = acetate; EDMA = ethylenediaminemonoacetic acid; HEEDTA = hydroxyethylethylenediamine triacetic acid and

$K_{es} = K_{\text{electrostatic}}$

Comparing these value of  $k$  (obtained from equation 14) with  $k_{\text{expt}}$  (Table IV.5) it can be concluded as was done earlier by Rorabacher and Margerum<sup>7</sup> and also by Kumar and Nigam<sup>8</sup> that, in all probability, the rate determining step is where three nitrogens of Trien and the acetate of aminocarboxylate is coordinated to  $Ni^{2+}$ . A higher rate than obtained from the above calculation was observed in case of DTPA. According to Rorabacher and Margerum an increase in number of similar donor atoms on the incoming ligand should increase the reaction rate. Because DTPA has eight donor atoms, an increase in the reaction rate could be expected when HEEDTA is replaced by DTPA in the reaction with  $Ni(II)$ -amine complex. The rate determining step appears to be the loss of a water molecule followed by coordination of the first nitrogen of aminocarboxylate.



## CHAPTER V

### KINETICS AND MECHANISM OF LIGAND SUBSTITUTION REACTIONS OF TETRAETHYLENEPENTAMINE AND TRI- ETHYLENETETRAMINE COMPLEXES OF NICKEL(II) WITH 4-(2-PYRIDYLAZO) RESORCINOL(PAR) USING STOPPED FLOW SPECTROPHOTOMETER

#### ABSTRACT

Kinetics and mechanism of ligand substitution reactions of the tetraethylenepentamine nickel(II) (Ni Tet) and the triethylenetetramine nickel(II) (Ni Trien) complexes with 4-(2-pyridylazoresorcinol (PAR, further abbreviated as  $H_2R$ ) have been studied spectrophotometrically at  $I = 0.1M$  ( $NaClO_4$ ) and  $25^\circ C$ . In both systems two distinct reaction steps are observed. The polyamine chelates of nickel react rapidly with Par to form an intermediate ternary complex  $Ni(Par)(Tet)$  or  $Ni(Par)(Trien)$ , which undergoes subsequent unwrapping of polyamine to give the final product

$Ni(Par)_2$ . The first step of the reaction follows the rate law:  $d[Ni(polyamine)(Par)]/dt = k_1 [Ni(polyamine)][Par]$ . The formation ternary complexes of  $Ni(polyamine)$  with Par has been investigated under second order equal concentration conditions. The values of

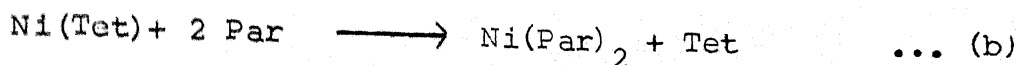
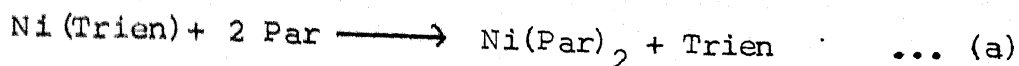
second order rate constants for Tet and Trien reactions are  $(2.1 \pm 0.2) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$  and  $7.8 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$  at pH = 9.0, I=0.1M and temp. = 25°C respectively.

The rate law for the second step is independent of Par concentration and written as  $d[\text{Ni}(\text{Par})_2]/dt = k_2[\text{Ni}(\text{polyamine})(\text{Par})]$ . Values of  $k_2$  for Trien and Tet systems are  $(2.5 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$  and  $(4.74 \pm 0.3) \times 10^{-5} \text{ s}^{-1}$  respectively. Effect of hydrogen ion concentration for both the reaction steps has been investigated and activation parameters have also been calculated.

#### V.1 INTRODUCTION

The mechanism of nickel polyamine formation and dissociation reactions has been thoroughly studied<sup>1-5</sup>. Ligand exchange reactions involving nickel-polyamines and aminocarboxylates<sup>6-10</sup> have been investigated and shown to proceed through the formation of a number of intermediates having both ligands coordinated to the central metal ion. These reactions are very sensitive to steric effects.

Steinhaus et al.<sup>11</sup> have studied the reaction of 1,10 phenanthroline and triethylenetetraamine nickel(II) and have demonstrated the formation of a mixed ligand intermediate viz.  $\text{Ni}(\text{Trien})(\text{Phen})$  in their study. In this investigation the kinetics of reactions (a) and (b) have been investigated to obtain a better understanding of the ligand substitution processes involving multidentate ligands.



Mixed ligand intermediates are formed as polyamine dissociates, allowing the effect of coordinated aromatic nitrogens of Par upon the dissociation of polyamine to be investigated and interpreted.

## V.2 EXPERIMENTAL SECTION

All chemicals were of AR Grade. Triethylenetetraamine (Trien) obtained from Fluka and Tetraethylenepentaamine AR(BDH) were purified by distillation under reduced pressure and standardised by pH-metric titration. Nickel-polyamine complexes were prepared by the addition of a slight excess of a standard solution of nickel perchlorate to a solution of polyamine and raising the pH to 10.5 by the addition of NaOH. The excess metal was filtered off as  $\text{Ni}(\text{OH})_2$  using a 0.22  $\mu\text{m}$  millipore filter. Concentration of Ni-polyamine complexes were obtained spectrophotometrically by adding excess cyanide to aliquotes of complexes resulting in formation of  $\text{Ni}(\text{CN})_4^{2-}$  and measuring its absorbances at 267 nm ( $\epsilon_{\text{Ni}(\text{CN})_4^{2-}} = 1.16 \times 10^4$ ) or at 285 nm ( $\epsilon_{\text{Ni}(\text{CN})_4^{2-}} = 4.63 \times 10^3$ )<sup>7-11</sup>. The mono sodium salt of 4-(2-pyridyl azo) resorcinol obtained from Reidel, Germany was used after recrystallisation from aqueous ethanol. Sodium tetraborate AR (BDH) and Boric acid AR (BDH) were used, wherever indicated, to prepare buffers of desired pH values.

Sodium perchlorate AR (E Merck, Germany) was used to maintain ionic strength of solutions at 0.1M.

All absorption measurements were made on a Toshniwal Spectrophotometer (Beckmann DU Type) model RL-02 which was equipped with a thermostated cell compartment. A stopped flow spectrophotometer model SF-3A from Hitech, England coupled with an ECIL storage oscilloscope model OS-768S was used to record kinetic traces for studying fast reactions. A polaroid camera was used to photograph these traces. An Elico Digital pH meter model LI-120 was used to record the pH of solutions.

### V.3 KINETIC MEASUREMENTS

The kinetics of the ligand substitution reaction between the nickel complex and par was studied at 495 nm ( $\lambda_{\max}$  of  $\text{Ni}(\text{Par})_2$ ) under pseudo first order conditions and pseudo first order rate constants were calculated from plots of  $\log (A_{\infty} - A_t)$  vs  $t$ . The conditions for experiment were pH = 9.0, I = 0.1M ( $\text{NaClO}_4$ ) and temp. = 25° or 30°C.

### V.4 RESULTS

#### V.4.1 Ligand substitution Reaction of $\text{NiTet}^{2+}$ with Par:

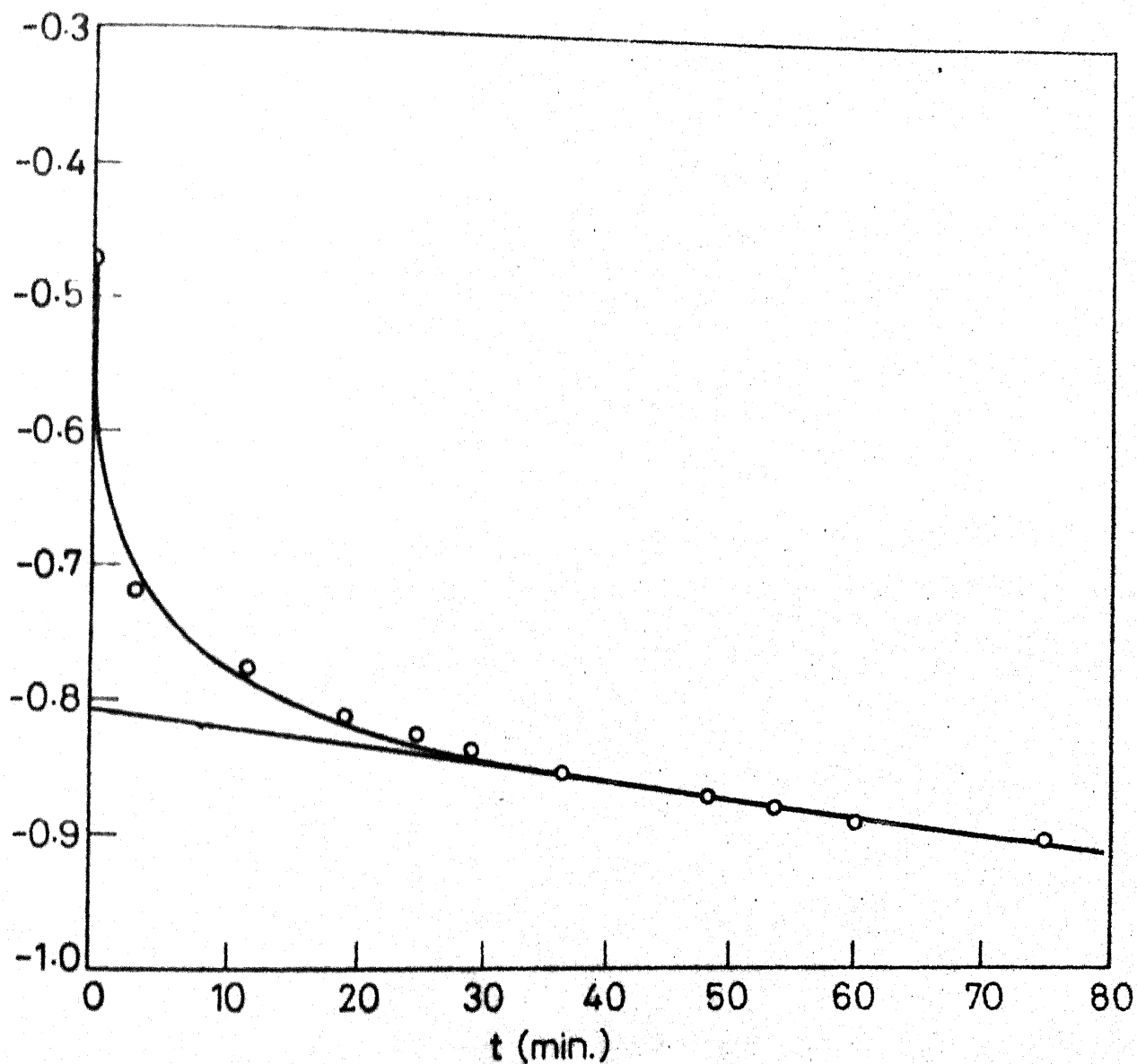
Under the experimental conditions stated above nickel and par form a 1:2 complex,  $\text{Ni}(\text{Par})_2$ . The dominant species of Par between pH 7 to 10 is the monoprotonated species  $\text{HR}^-$  as is evident from the values of protonation constants of par<sup>13</sup>. The

molar absorption coefficients of  $\text{Ni}(\text{Par})_2$  and  $\text{Hpar}$  at 495 nm are  $8.1 \times 10^4$  and  $1.6 \times 10^3$  respectively<sup>12,13</sup>. Taking par in a sufficient excess over the nickel complex so that the reaction can be regarded as pseudo first order in  $\text{Ni}(\text{Tet})^{2+}$ , plots of  $\log(A_\infty - A_t)$  vs  $t$  gave two distinct portions. A typical plot is given in Fig. V.1. The first part is due to a faster reaction and second due to a slower one. Extrapolation of the linear portion (due to slower reaction) to zero time gives an absorption  $A_1$  which is higher than what would be expected immediately after mixing the reactants. This points to the formation of an intermediate during the course of reaction and the first steep portion of the curve indicates rapid formation of this intermediate. The pseudo first order rate constants for the faster step were calculated taking  $A_1$ , obtained above, as  $A_\infty$  for the faster step.

Thereafter, the fast reaction was studied under second order equal concentration conditions on stopped flow spectrophotometer. Rate data gave excellent second order plots of  $(A'_\infty - A_t)^{-1}$  vs  $t$  (Fig. V.2).  $A'_\infty$  corresponds to the absorbance after complete formation of  $\text{Ni}(\text{Polyamine})(\text{Par})$ . This indicates first order dependence with respect to both Par and NiTet complex and points to the formation of a mixed ligand complex i.e.  $\text{Ni}(\text{Tet})(\text{Par})$  with the following rate law

$$\frac{d [\text{Ni}(\text{Tet})(\text{Par})]}{dt} = k_1 [\text{NiTet}]_T [\text{Par}]_T \quad \dots (1)$$

where  $[\text{Ni Tet}]_T$  and  $[\text{Par}]_T$  represent the total concentration of protonated and unprotonated forms of  $\text{Ni}(\text{Tet})^{2+}$  and



V.1 Plot of a typical kinetic run for the reaction of  $\text{Ni}(\text{Tet})^{2+}$  with par.  $[\text{Ni}(\text{Tet})^{2+}]_T = 2.0 \times 10^{-6} \text{ M}$ ,  $[\text{Par}]_T = 5.0 \times 10^{-5} \text{ M}$ .  
temp. =  $25^\circ\text{C}$ , pH = 9.0 and  $I = 0.1\text{M}$ .

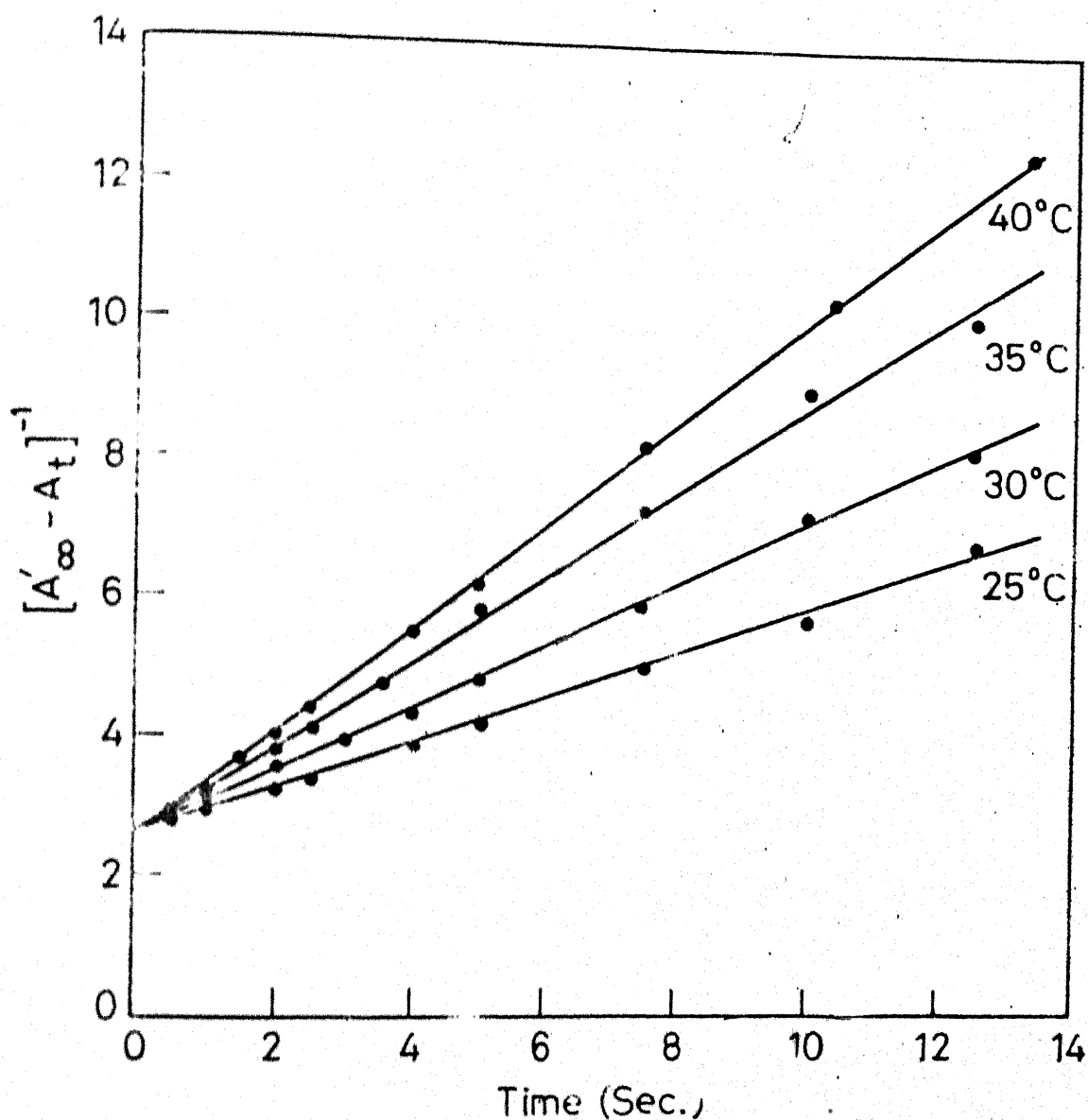


Fig. V.2 Second order plots for the formation of  $\text{Ni}(\text{Tet})(\text{Par})$  at different temperatures. A plots of  $[\text{A}'_{\infty} - \text{A}_t]^{-1}$  Vs  $t$ .  
 $[\text{Ni Tet}] = [\text{Par}] = 1.5 \times 10^{-5} \text{ M}$ ,  $\text{pH} = 9.0$ ,  $I = 0.1 \text{ M}$

Par respectively. In further treatment Par is further abbreviated as  $H_2R$ .

#### V.4.2 Effect of pH

A series of kinetic runs were taken in a large pH range in order to determine the effect of hydrogen ion concentration on the fast reaction. It was observed that the rate increases with increase of pH above 8.5 (Table V.1, Fig. V.3). Assuming

Table V.1. Effect of pH on the formation of mixed ligand ternary complex  $Ni(Tet)(Par)^*$

$[Ni(Tet)^{2+}]_T = [Par]_T = 1.5 \times 10^{-5} M$ ,  $I = 0.1 M$ ,  
temp. =  $25^\circ C$ .

pH	$10^{-4} \times k_2, M^{-1} S^{-1}$	pH	$10^{-4} \times k_2, M^{-1} S^{-1}$
7.5	1.18	9.52	2.40
8.1	1.20	9.90	3.24
8.63	1.23	10.40	8.80
8.74	1.37	10.55	11.2
8.9	1.40		

\* under second order equal concentration conditions.

the existence of protonated and unprotonated forms of Par (Fig. V.4) and Ni Tet (Fig. V.5), the following rate equation (2) is postulated.



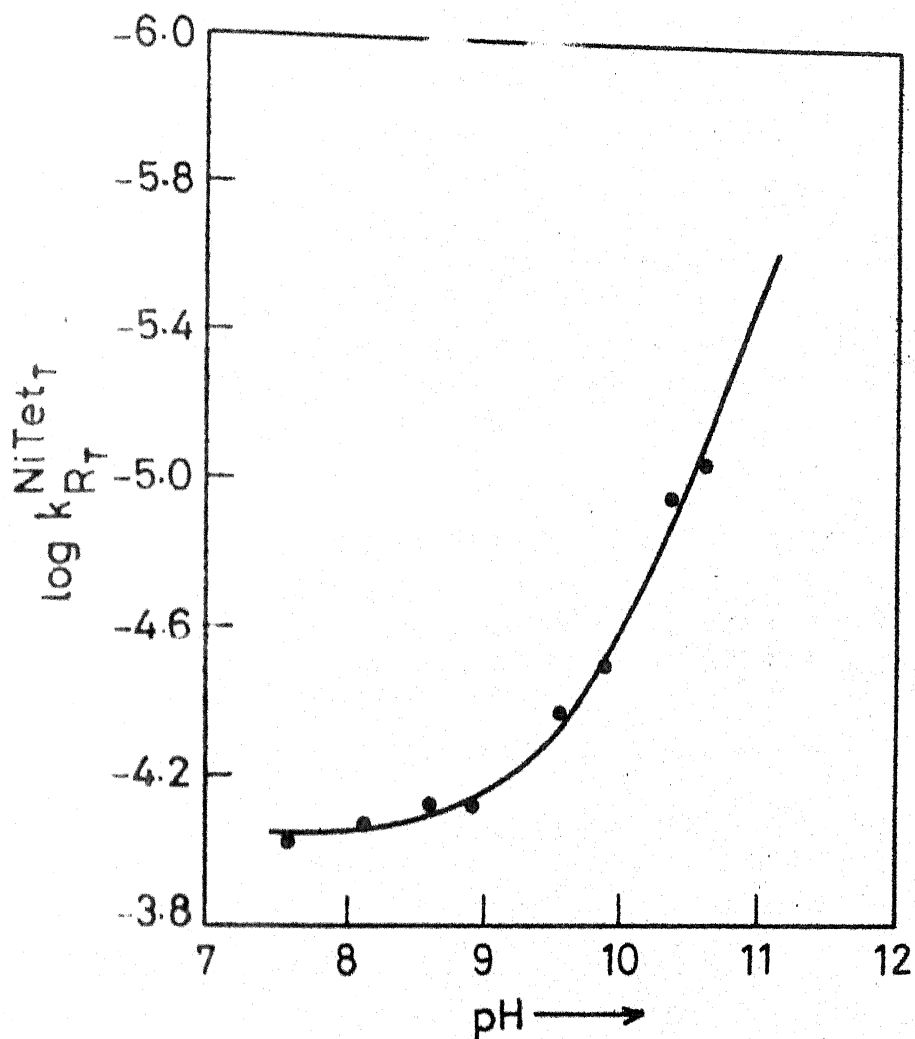


Fig. V.3 Fit of theoretical curve to experimental rate constants for the reaction of NiTet with Par. temp. = 25°C and  $I = 0.1M$ .

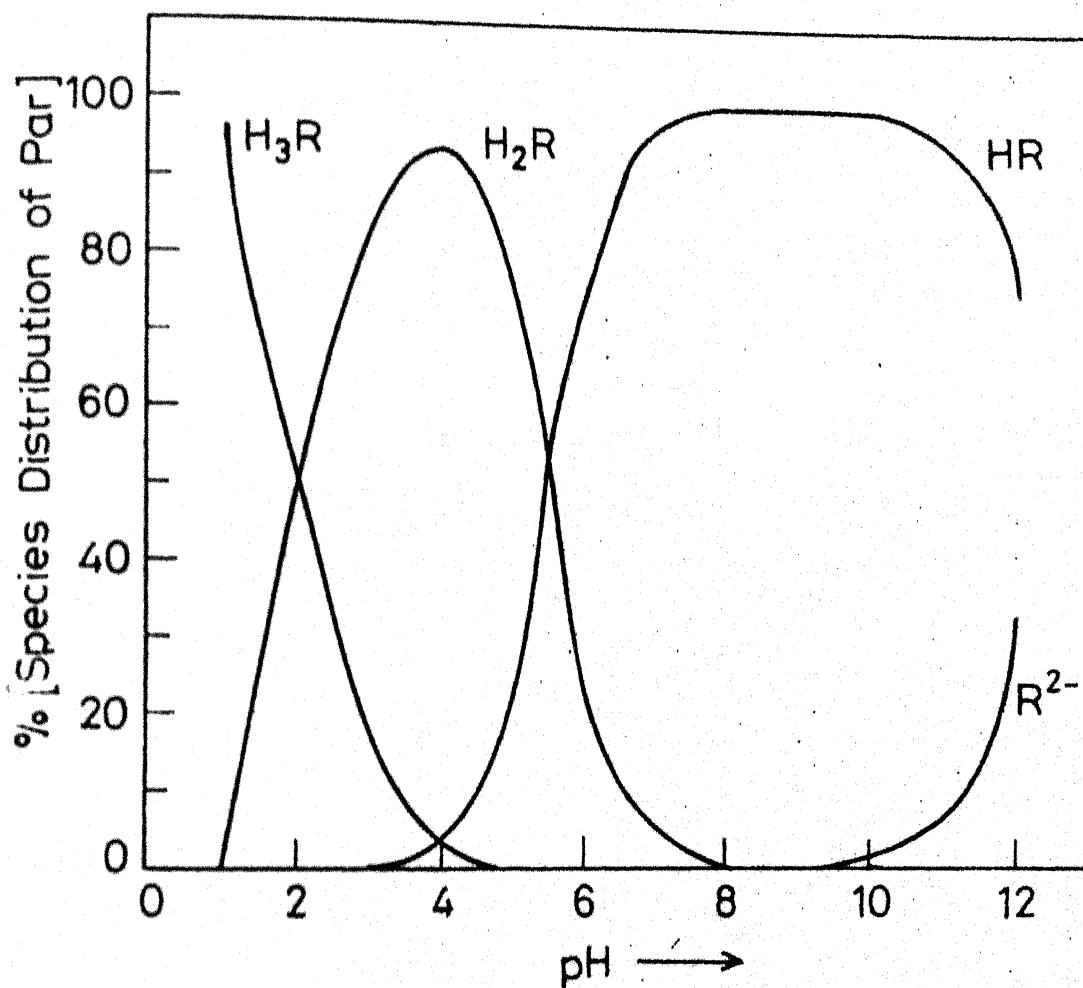


Fig. V.4 Species distribution of Par as a function of pH;  $[Par] = 5.0 \times 10^{-5} M$ .

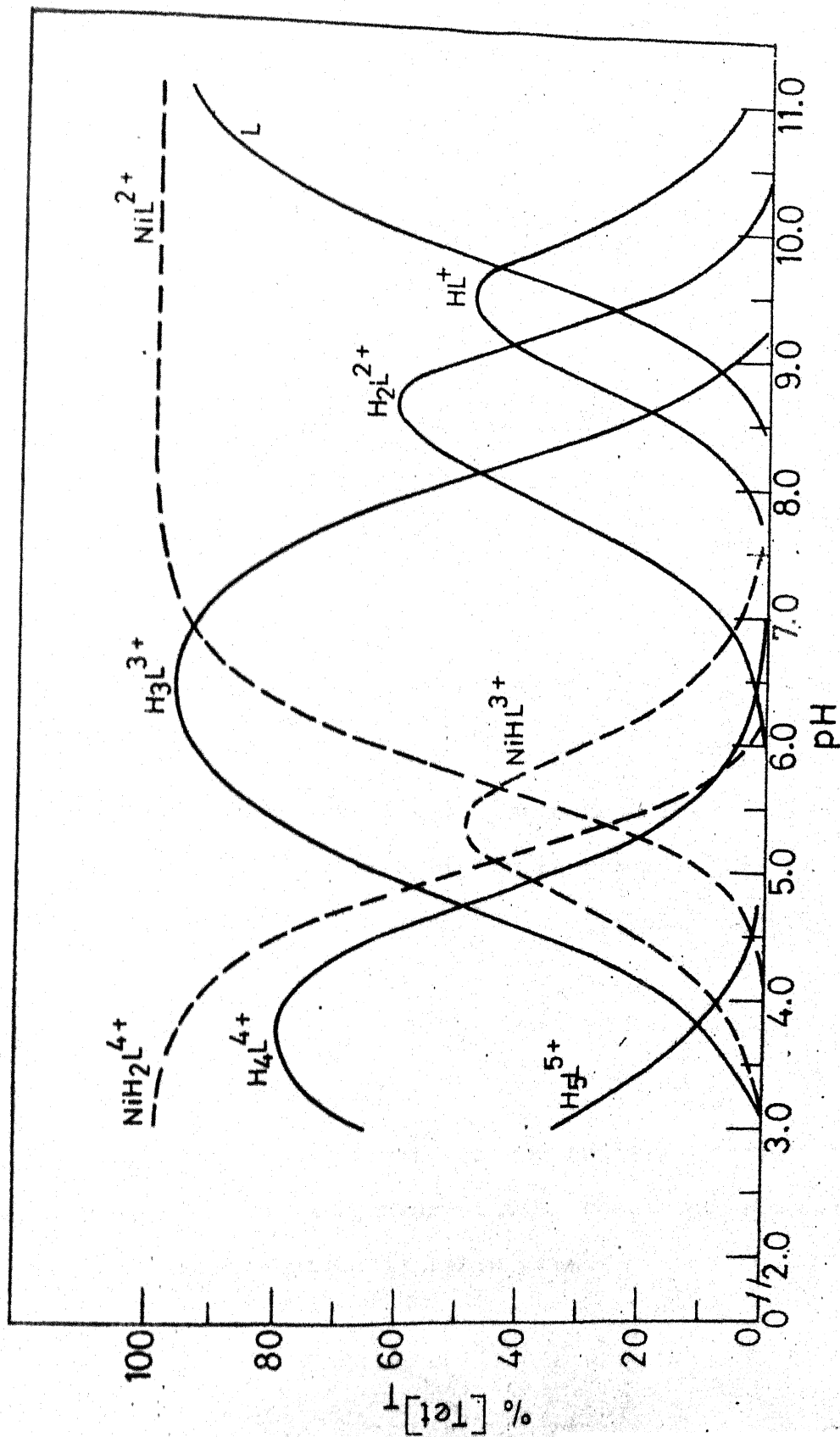


Fig.V.5 Species distribution of Tet and NiTet as a function of pH;  
 $[\text{Ni}^{2+}] = [\text{Tet}] = 5.0 \times 10^{-4} \text{ M}$ .

$$\begin{aligned} \text{rate} &= k_{R_T}^{\text{NiTet}} [\text{NiTet}]_T [\text{R}^{2-}]_T \\ &= (k_R + k_{HR} K_{HR} [\text{H}^+]) [\text{NiTet}] [\text{R}^{2-}] \quad \dots (2) \end{aligned}$$

$$\text{or } k_{R_T}^{\text{NiTet}} \cdot \frac{[\text{NiTet}]_T}{[\text{NiTet}^{2+}]} \cdot \frac{[\text{R}]_T}{[\text{R}^{2-}]} = k_R + k_{HR} K_{HR} [\text{H}^+] \quad \dots (3)$$

$$\text{where } \frac{[\text{NiTet}]_T}{[\text{NiTet}^{2+}]} = 1 + K_{\text{NiHTet}}^{\text{NiTet}} [\text{H}^+]$$

$$\text{and } \frac{[\text{R}]_T}{[\text{R}^{2-}]} = 1 + K_{HR} [\text{H}^+] + K_{HR} K_{H_2R} [\text{H}^+]^2 + \dots$$

A plot of left hand side of equation (3) versus  $[\text{H}^+]$  gives a straight line (Fig. V.6) with an intercept  $k_R = 7.7 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$  and a slope  $k_{HR} K_{HR} = 2.2 \times 10^{16}$  or  $k_{HR} = 1.1 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ . The solid curve in Fig. V.3 is calculated from the resolved rate constants and relevant pk's of the reactants. The agreement between the theoretical curve and experimental points is quite good.

#### V.4.3 Effect of Temperature

The activation parameters for the faster reaction were calculated from the Arrhenius plot in the temperature range  $25^\circ - 45^\circ\text{C}$  and are given in Table V.2A.

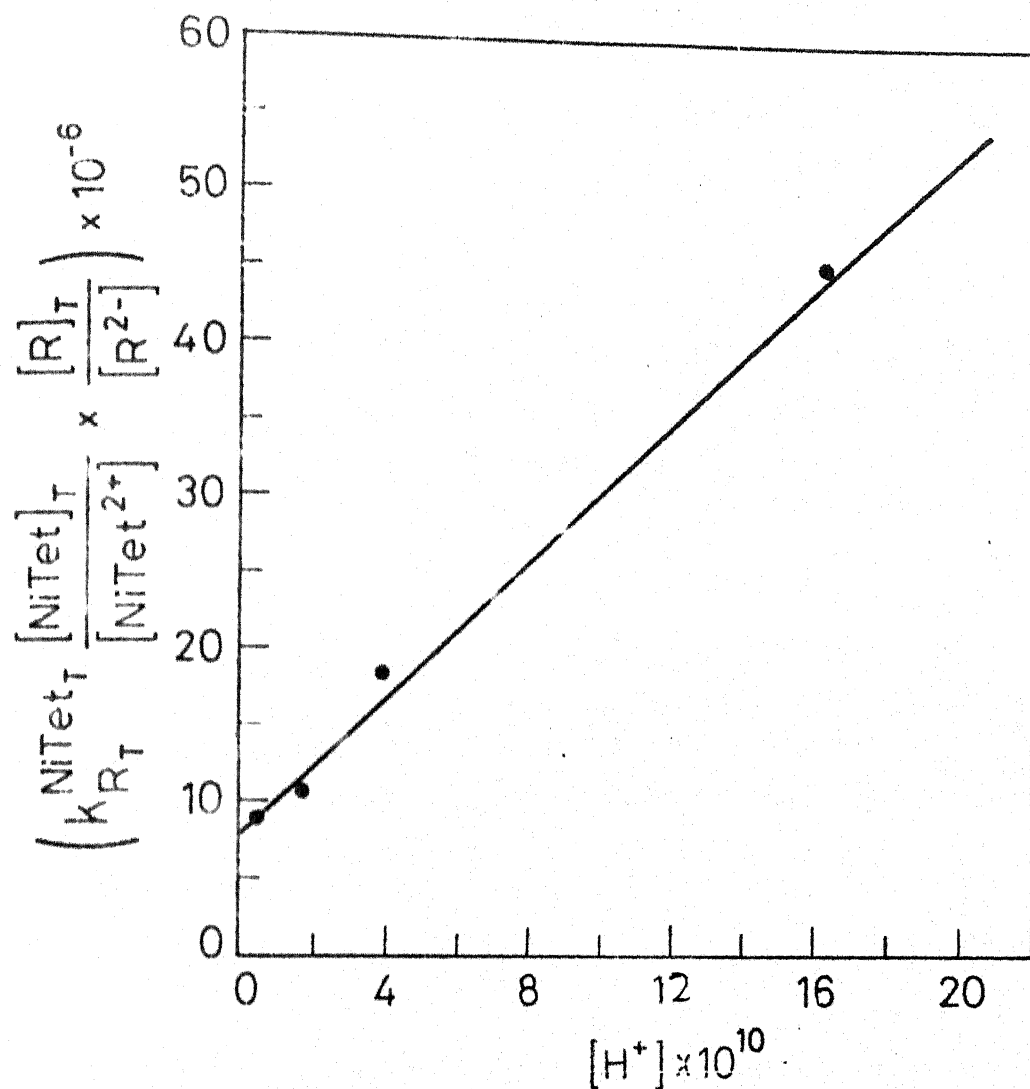


Fig. V.6 Resolution of the rate constant for the formation of Ni(Tet)(Par). temp. = 25°C and I = 0.1M.

Table V.2. Effect of temperature on the reaction of Par with Ni(tetren) complex.

pH = 9.0±0.1 (Buffered with Borax-Boric acid), I=0.1M

A. Formation of ternary complex  
Ni(Tet)(Par)

$$[\text{NiTet}^{2+}]_T = [\text{Par}]_T = 1.5 \times 10^{-5} \text{M}$$

$$E_a = 11.4 \text{ kcal mole}^{-1}$$

$$\Delta H^\ddagger = 10.8 \text{ kcal mole}^{-1}$$

$$pZ = 6.5 \times 10^{11} \text{ cm}^{-1}$$

$$\Delta S^\ddagger = 2.2 \text{ e.u.}$$

B. Formation of Ni(Par)<sub>2</sub> from  
Ni(Tet) and Par

$$[\text{NiTet}^{2+}]_T = 2.0 \times 10^{-6} \text{M},$$

$$[\text{Par}] = 1.0 \times 10^{-4} \text{M}.$$

$$E_a = 14.2 \text{ kcal mole}^{-1}$$

$$\Delta H^\ddagger = 13.6 \text{ kcal mole}^{-1}$$

$$pZ = 4.35 \times 10^5 \text{ cm}^{-1}$$

$$\Delta S^\ddagger = -37 \text{ e.u.}$$

#### V.5 Conversion of Ni(Tet)Par into Ni(Par)<sub>2</sub>

The slow reaction between Ni(Tet)(Par) and Par was studied at various par concentrations under pseudo first order conditions and it was observed that the reaction is independent of Par concentration and is first order in Ni(Tet)(Par) in accordance with rate equation (4).

$$\text{rate} = \frac{d[\text{Ni(Par)}_2]}{dt} = k_2 [\text{Ni(Tet)(Par)}] \quad \dots (4)$$

All rate constants along with reaction conditions are given in Table V.3.

Table V.3. First order rate constants for the formation of  $\text{Ni}(\text{Par})_2$  from  $\text{Ni}(\text{Tet})(\text{Par})$ .

$$[\text{NiTet}^{2+}]_T = (2-5) \times 10^{-6} \text{M}, \text{pH}^a = 9.0 \pm 0.1,$$

$$I = 0.1\text{M} (\text{NaClO}_4), \text{temp.} = 25^\circ\text{C}.$$

$10^5 \times [\text{Par}]_T$ , M	$10^5 \times k_{\text{obsd}}$ $\text{s}^{-1}$	$10^5 \times [\text{Par}]_T$ , M	$10^5 \times k_{\text{obsd}}$ $\text{s}^{-1}$
8.0	5.30	4.0	4.50
7.5	5.20	3.0	4.60
6.0	4.78	2.5	4.60
5.0	4.60	2.0	4.50

$$k_{\text{obsd}}(\text{av}) = (4.74 \pm 0.3) \times 10^{-5} \text{sec}^{-1}$$

a. Borax-boric acid buffer.

#### V.5.1 Activation Parameters

Activation parameters were also calculated using Arrhenius plot in the temperature range  $25^\circ\text{--}40^\circ\text{C}$  and are given in Table V.2B.

#### V.5.2 Effect of hydrogen ion concentration

The reaction was studied in the pH range 7-10 and it was observed that the rate increases with decrease of pH below 8. (Table V.4, Fig. V.7). This behaviour may be due to higher dissociation rate of protonated form of  $\text{Ni}(\text{Tet})(\text{Par})$  compared to that of unprotonated one, which is generally true for many protonated complexes.

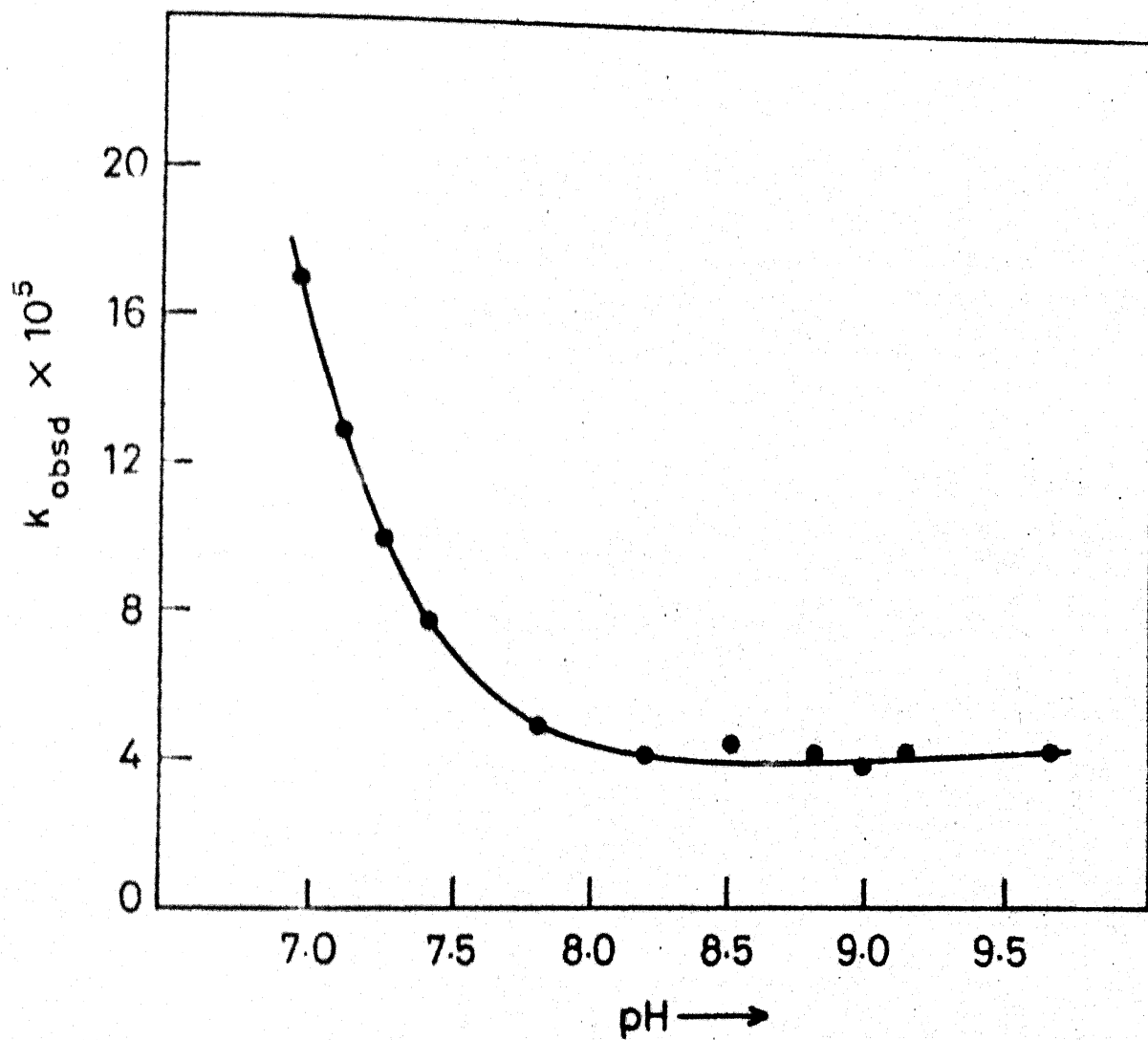


Fig.V.7 Effect of hydrogen ion concentration on the dissociation of  $\text{Ni(Tet)(Par)}$ ; temp. =  $25^\circ\text{C}$  and  $I=0.1\text{M}$ .



Table V.4. Effect of pH<sup>a</sup> on the first order rate constants for the formation of Ni(Par)<sub>2</sub> from Ni(Tet)(Par).

$$[\text{Ni}(\text{Tet})^{2+}]_{\text{T}} = 4.15 \times 10^{-6} \text{M}, [\text{Par}]_{\text{T}} = 1.0 \times 10^{-4} \text{M},$$

$$I = 0.1 \text{M} (\text{NaClO}_4); \text{temp.} = 25 \pm 0.1^\circ \text{C}$$

pH	$10^5 k_{\text{obsd}},$ $\text{sec}^{-1}$	pH	$10^5 k_{\text{obsd}},$ $\text{sec}^{-1}$
6.98	$17.3 \pm 0.4$	8.20	$4.6 \pm .05$
7.10	$13.0 \pm 0.1$	8.55	$4.5 \pm 0.2$
7.25	$9.9 \pm .05$	8.80	$5.0 \pm 0.1$
7.40	$7.7 \pm 0.1$	9.00	$4.9 \pm 0.1$
7.85	$6.6 \pm 0.2$	9.15	$4.6 \pm 0.2$
		9.80	$5.0 \pm 0.1$

a. Borax-boric acid buffer.

#### V.6 Ligand Substitution Reaction of Ni(Trien)<sup>2+</sup> Complex with Par

Two distinct steps were observed again in the reaction of par with Ni(Trien)<sup>2+</sup>, as in the case of Ni(Tet)<sup>2+</sup>. The first is the formation of a ternary complex, Ni(Trien)(Par), which is first order with respect to both Ni(Trien) and Par studied under pseudo first order conditions (Table V.5) and also under second order equal concentration conditions on a stopped flow spectrophotometer (Fig.V.8). The second step in the reaction is the conversion of

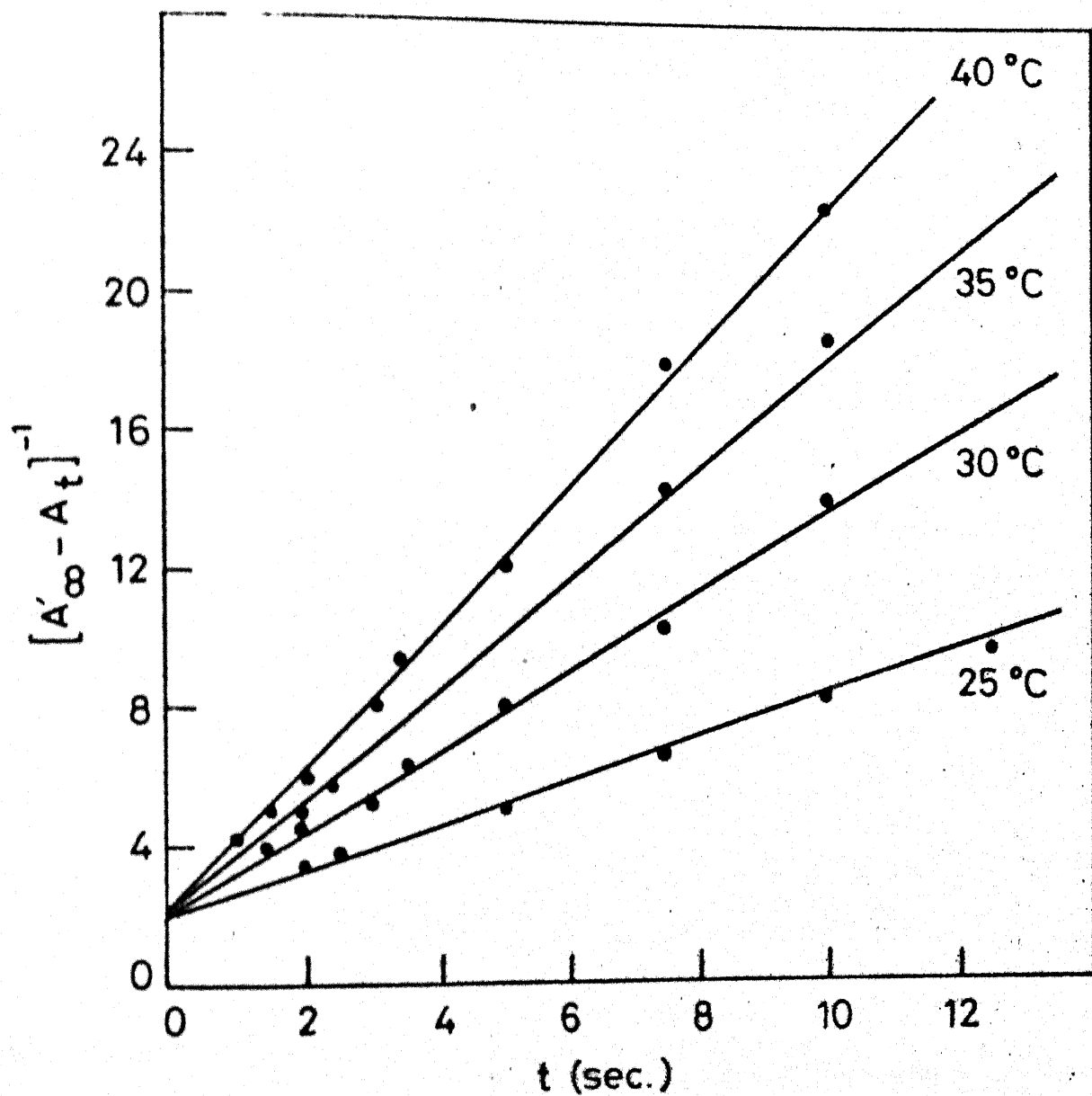


Fig. V.8 Second order plots for the formation of  $[\text{Ni}(\text{trien})(\text{Par})]$  at different temperatures. Plots of  $[A'_\infty - A_t]^{-1}$  vs  $t$ .  $[\text{Ni}(\text{trien})] = [\text{Par}] = 5.0 \times 10^{-6} \text{ M}$ ,  $\text{pH} = 9.0$ ,  $I = 0.1 \text{ M}$ .

Table V.5. Effect of par concentration on the formation of  $\text{Ni}(\text{Trien})(\text{Par})$ , under pseudo first order conditions.  
 $[\text{Ni}(\text{Trien})^{2+}]_T = (2-8) \times 10^{-6} \text{ M}$ ,  $\text{pH} = 10.6$ ,  $\text{temp.} = 30^\circ \text{C}$ ,  
 $I = 0.1 \text{ M } (\text{NaClO}_4)$ .

$10^5 \times [\text{Par}]_T, \text{M}$	$k_{\text{obsd}}, \text{sec}^{-1}$	$k_{R_T}^{\text{NiT}} \times 10^{-4}, \text{M}^{-1} \text{S}^{-1}$
10.0	8.10	8.10
7.50	6.50	8.66
6.0	4.71	7.85
5.0	3.90	7.80
5.0	3.85	7.70
4.0	3.30	8.25
3.0	2.40	8.00
2.0	1.70	8.50
1.0	0.80	8.00

$$k_{R_T}^{\text{NiT}} (\text{av}) = (8.10 \pm 0.32) \times 10^4, \text{M}^{-1} \text{S}^{-1}$$

mixed ligand complex,  $\text{Ni}(\text{Trien})(\text{Par})$ , to  $\text{Ni}(\text{Par})_2$  which is first order with respect to  $\text{Ni}(\text{Trien})(\text{Par})$  and independent of concentration of Par (Table V.6).

#### V.6.1 Effect of pH

Formation of the ternary complex was studied at various hydrogen ion concentrations and it was observed that the rate

Table V.6. First order Rate Constant for the Formation of  $\text{Ni}(\text{Par})_2$  from  $\text{Ni}(\text{Trien})(\text{Par})$ .

$[\text{Ni}(\text{Trien})^{2+}]_T = (2-5) \times 10^{-6} \text{M}$ ,  $\text{pH}^a = 9.0 \pm 0.1$   
 $I = 0.1\text{M}$ ,  $\text{temp.} = 30^\circ\text{C}$ .

$10^5 \times [\text{Par}]_T,$ M	$10^4 \times k_{\text{obsd}},$ $\text{sec}^{-1}$
9.0	2.45
7.5	2.50
6.0	2.40
5.6	2.60
3.5	2.60
2.5	2.40

$$k_{\text{obsd}} (\text{av}) = (2.5 \pm 0.1) \times 10^{-4} \text{ sec}^{-1}$$

a. Borax-boric acid buffer.

increases with increase of pH above 8.5 (Fig. V.9, Table V.7).

The rate equation for the formation of  $\text{Ni}(\text{Trien})(\text{Par})$  is given by

$$\frac{d [\text{Ni}(\text{Trien})(\text{Par})]}{dt} = k_{R_T}^{\text{NiT}} [\text{NiT}]_T [\text{Par}]_T \quad \dots (5)$$

where  $\text{NiT}$  represents Nickel-Trien complex.

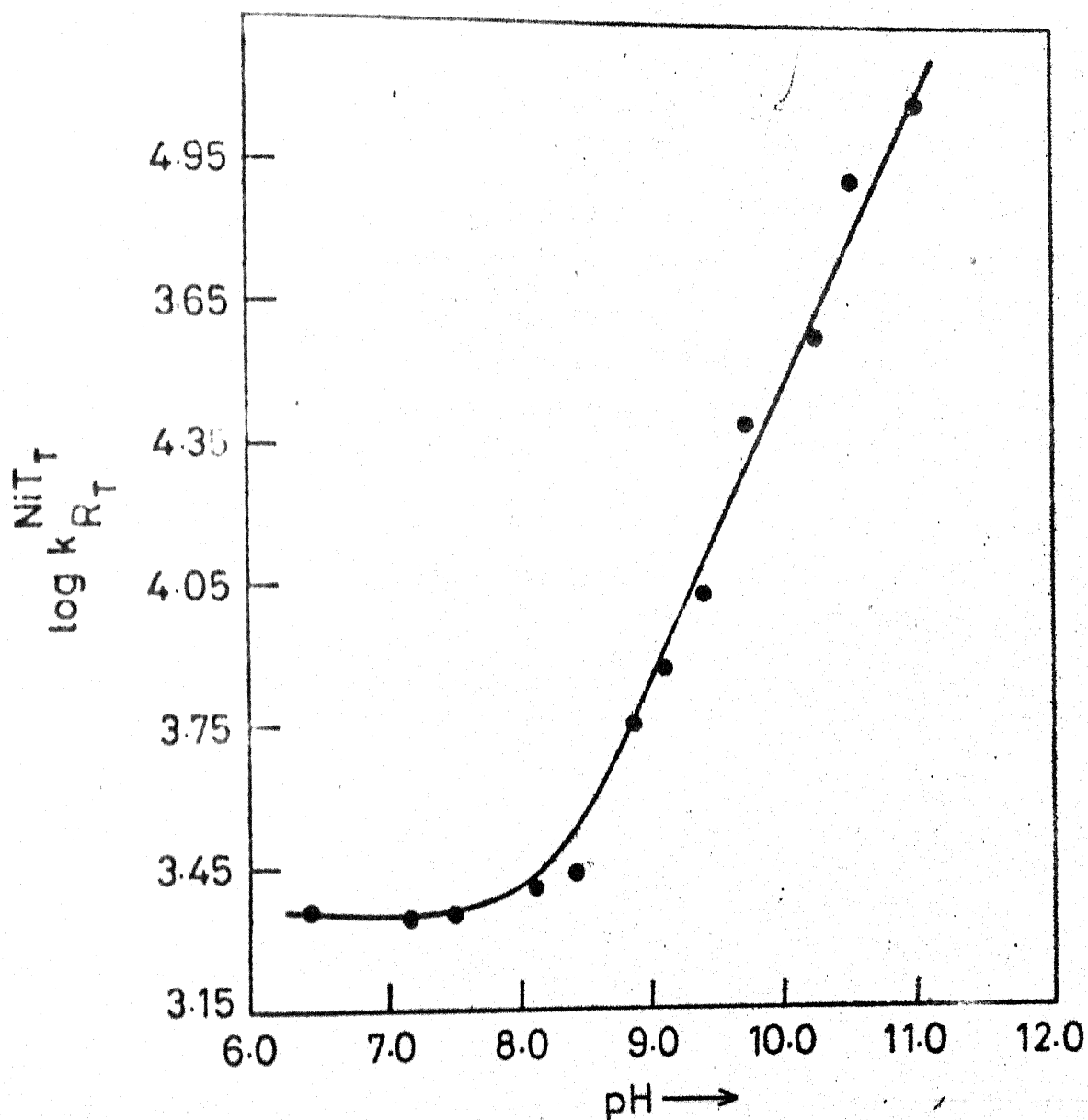


Fig. V-9 Effect of pH on the formation of Ni(Trien)(Par). Solid line calculated from the resolved rate constants.

Table V.7. Effect of pH<sup>a</sup> on the formation of ternary complex  
Ni(Trien)(Par)

$$[\text{Ni}(\text{Trien})^{2+}]_T = 4.0 \times 10^{-6} \text{M}, [\text{Par}]_T = 4.0 \times 10^{-5} \text{M},$$

$$I = 0.1 \text{M}, \text{temp.} = 25^\circ \text{C}$$

pH	$k_{\text{obsd}}$	$k_{R_T}^{\text{NiT}_T} = \frac{k_{\text{obsd}}}{[\text{Par}]_T}, \text{M}^{-1}\text{S}^{-1}$
6.4	0.090	$2.25 \times 10^3$
6.7	0.08	$2.00 \times 10^3$
7.1	0.09	$2.25 \times 10^3$
7.5	0.092	$2.30 \times 10^3$
8.1	0.086	$2.15 \times 10^3$
8.37	0.11	$2.75 \times 10^3$
8.7	0.19	$4.75 \times 10^3$
9.1	0.30	$7.5 \times 10^3$
9.42	0.44	$1.10 \times 10^4$
9.7	0.69	$1.72 \times 10^4$
10.00	1.49	$3.72 \times 10^4$
10.53	3.30	$8.25 \times 10^4$
11.0	5.28	$13.2 \times 10^4$

a. Borax boric acid buffer.

The right hand side of above equation can, by making use of protonation constants of Par and stability constant of NiT(OH), be equated as

$$\begin{aligned}
 k_{R_T}^{NiT} [NiT]_T [R]_T &= k_{H_2R}^{NiT} [H_2R] [NiT^{2+}] + k_{HR}^{NiT} [HR^1] [NiT^{2+}] \\
 &+ k_{HR}^{NiT(OH)} [HR^1] [NiT(OH)] + k_R^{NiT(OH)} [R^{2-}] [NiT(OH)] \\
 &+ k_R^{NiT} [NiT^{2+}] [R^{2-}] \quad \dots (6)
 \end{aligned}$$

In the pH range 6-7.5, calculations for species distribution (Fig. V.4 and Fig. IV.1 suggest that the terms containing NiT(OH) and  $R^{2-}$  can be neglected and equation (6) transforms to equation (7) or (8).

$$\begin{aligned}
 k_{R_T}^{NiT} [NiT]_T [R]_T &= k_{H_2R}^{NiT} [H_2R] [NiT^{2+}] + k_{HR}^{NiT} [HR^1] [NiT^{2+}] \quad \dots (7) \\
 &= (k_{H_2R}^{NiT} K_{H_2R} K_{HR} [H^+]^2 + k_{HR}^{NiT} K_{HR} [H^+]) [R^{2-}] [NiT^{2+}] \quad \dots (8)
 \end{aligned}$$

Equation (8) can be rearranged to equation (9)

$$\begin{aligned}
 k_{R_T}^{NiT} \frac{[NiT]_T}{[NiT^{2+}]} \cdot \frac{[R]_T}{[R^{2-}]} \cdot \frac{1}{[H^+]} &= k_{H_2R}^{NiT} K_{H_2R} K_{HR} [H^+] \\
 &+ k_{HR}^{NiT} K_{HR} \quad \dots (9)
 \end{aligned}$$

The plot of left hand side of equation(9) vs  $[H^+]$  yields a straight line (Fig.V.10) with an intercept  $= k_{HR}^{NiT} K_{HR} = 4.56 \times 10^{15}$  and so ,  $k_{HR}^{NiT} = 2.28 \times 10^3 \text{ M}^{-2} \text{ S}^{-1}$

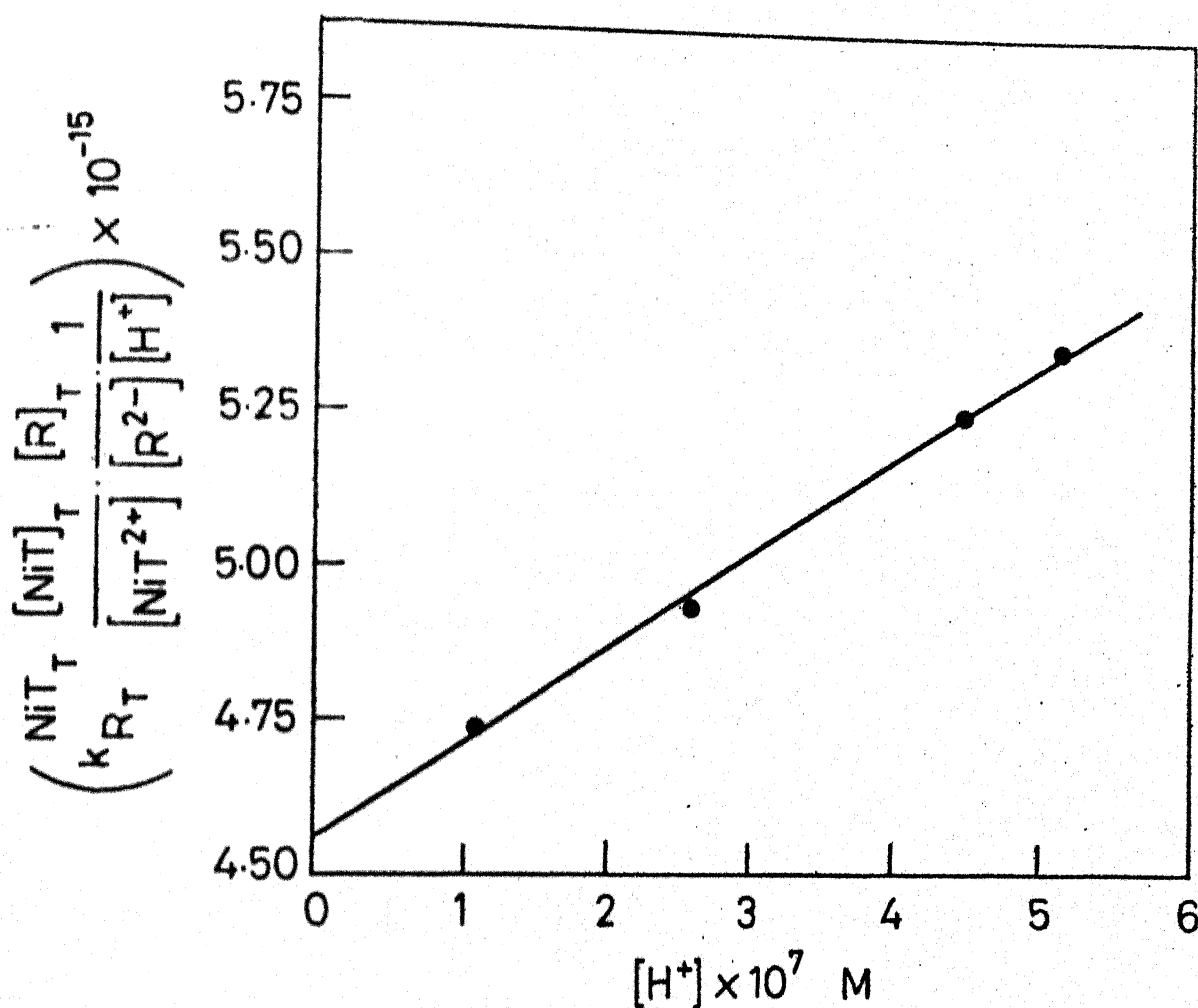


Fig.V.10 Resolution of the rate constant viz  $k_{H_2R}^{NiT}$  and  $k_{HR}^{NiT}$  for the formation of  $Ni(Trien)(Par)$ ; temp. =  $26^\circ C$  and  $I = 0.1M$ .



and slope =  $k_{H_2R}^{NiT} K_{H_2R} K_{HR} = 1.69 \times 10^{21}$  and so

$$k_{H_2R}^{NiT} = 2.67 \times 10^3 \text{ M}^{-3} \text{ S}^{-1}$$

Between pH 7.5 and 9.0, where  $HR^{1-}$  is the only important reactive specie (Fig. V.4), the term  $k_{HR}^{NiT(OH)}$  can be evaluated by applying correction for  $k_{HR}^{NiT}$  as

$$\begin{aligned} k_{R_T}^{NiT} \frac{[NiT]_T}{[NiT^{2+}]} \cdot \frac{[R]_T}{[R^{2-}]} &= k_{H_2R}^{NiT} K_{H_2R} K_{HR} [H^+]^2 + k_{HR}^{NiT} K_{HR} [H^+] \\ &= k_{HR}^{NiT(OH)} K_{HR} K_{NiT(OH)} [OH^-] [H^+] \end{aligned}$$

... (10)

Dividing by  $[H^+]$  throughout,

$$\begin{aligned} k_{R_T}^{NiT} \cdot \frac{[NiT]_T}{[NiT^{2+}]} \cdot \frac{[R]_T}{[R^{2-}]} \cdot \frac{1}{[H^+]} &= k_{H_2R}^{NiT} K_{H_2R} K_{HR} [H^+] + k_{HR}^{NiT} K_{HR} \\ &= k_{HR}^{NiT(OH)} K_{HR} K_{NiT(OH)} K_w \frac{1}{[H^+]} \end{aligned}$$

... (11)

or

$$A = k_{HR}^{NiT(OH)} K_{HR} K_{NiT(OH)} K_w \frac{1}{[H^+]} \quad \dots (12)$$

where A represents left hand side of Eqn. (11). The plot of 'A' vs  $1/[H^+]$  yields a straight line passing through the origin (Fig. V.11x) with a slope equal to

$$k_{HR}^{NiT(OH)} \cdot K_{HR} K_{NiT(OH)} K_w = 1.86 \times 10^7$$

and so  $k_{HR}^{NiT(OH)} = 2.95 \times 10^4$

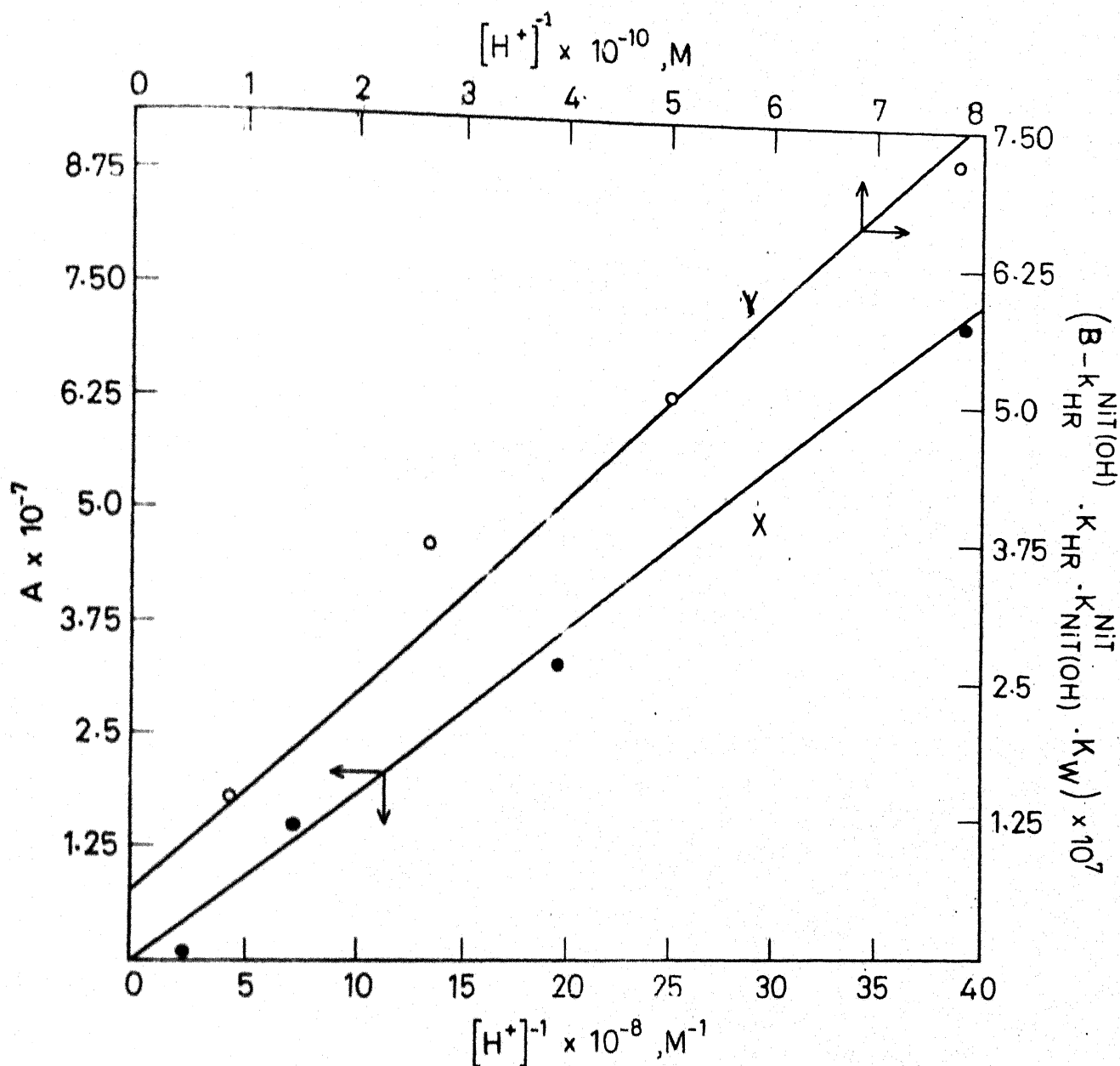


Fig. V-11 Resolution of the rate constant viz  $k_{HR}^{NiT(OH)}$ ,  $k_R^{NiT}$  and  $k_R^{NiT(OH)}$  for the formation of Ni(Trien)(Par); temp. = 25°C and  $I = 0.1M$ .

Above pH 9, the other two terms of Eqn. 6, can be obtained from the data at higher pH value by correcting for the contribution of protons using equation (6), which can be transformed by algebraic manipulation to equation (13) as

$$k_{R_T}^{NiT} \frac{[NiT]_T [R^-]_T}{[NiT^{2+}] [R^{2-}]} - \{ k_{H_2R}^{NiT} K_{H_2R} K_{HR} [H^+]^2 + k_{HR}^{NiT} K_{HR} [H^+] \} + k_{HR}^{NiT(OH)} K_{HR} k_{NiT(OH)}^{NiT} \cdot K_w = k_R^{NiT} + k_R^{NiT(OH)} k_{NiT(OH)}^{NiT} \frac{K_w}{[H^+]} \quad \dots (13)$$

or

$$B = k_{HR}^{NiT(OH)} K_{HR} k_{NiT(OH)}^{NiT} K_w = k_R^{NiT} + k_R^{NiT(OH)} k_{NiT(OH)}^{NiT} K_w \frac{1}{[H^+]} \quad \dots (14)$$

$$\text{where } B = k_{R_T}^{NiT} \frac{[NiT]_T}{[NiT^{2+}]} \cdot \frac{[R^-]_T}{[R^{2-}]} - k_{H_2R}^{NiT} K_{H_2R} K_{HR} [H^+]^2 - k_{HR}^{NiT} K_{HR} \cdot [H^+] \quad \dots (15)$$

$$\text{and } K_w = [OH^-] [H^+].$$

Thus a plot of left hand side of equation (14) vs  $1/[H^+]$  (Fig. V.11Y) gives an intercept  $k_R^{NiT} = 8.12 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$  and a slope  $k_R^{NiT(OH)} \cdot k_{NiT(OH)}^{NiT} \cdot K_w = 8.46 \times 10^{-4}$  and so

$$k_R^{NiT(OH)} = 2.67 \times 10^6 \text{ M}^{-1}\text{s}^{-1}.$$

All the resolved rate constants obtained from the treatment described above for Trien reaction are given in Table V.8 which also includes values for Tet system.

Table V.8. Resolved Rate Constants for the formation of Ternary Complexes, temp. = 25°C and I = 0.1M (NaClO<sub>4</sub>).

<u>Ni(Trien) - Par system</u>		<u>Ni(Tet) - Par system</u>	
$k_{H_2R}^{NiT}$	$= 2.67 \times 10^3 \text{ M}^{-1}\text{S}^{-1}$	$k_{HR}^{NiTet}$	$= 1.1 \times 10^4 \text{ M}^{-1}\text{S}^{-1}$
$k_{HR}^{NiT}$	$= 2.28 \times 10^3 \text{ M}^{-1}\text{S}^{-1}$	$k_R^{NiTet}$	$= 7.7 \times 10^6 \text{ M}^{-1}\text{S}^{-1}$
$k_{HR}^{NiT(OH)}$	$= 2.95 \times 10^4 \text{ M}^{-1}\text{S}^{-1}$		
$k_R^{NiT(OH)}$	$= 2.67 \times 10^6 \text{ M}^{-1}\text{S}^{-1}$		
$k_R^{NiT}$	$= 8.12 \times 10^6 \text{ M}^{-1}\text{S}^{-1}$		

Figure V.9 gives a plot of equation (6) using the above resolved rate constants. The good agreement between theoretical curve and experimental points gives confidence in the values of resolved rate constants determined by the procedure described above.

#### V.7 Formation of Ni(Par)<sub>2</sub> from Ni(Trien)(Par):

##### V.7.1 Effect of pH

The formation of Ni(Par)<sub>2</sub> from Ni(Trien)(Par) was studied under pseudo first order conditions at different hydrogen ion concentrations. The rate constants obtained at various pH values are given in Table V.9. The effect of [H<sup>+</sup>] was found to be negligible.

Table V.9. Effect of pH on the Formation rate constant for  $\text{Ni}(\text{Par})_2$  from  $\text{Ni}(\text{Trien})(\text{Par})$ .

$[\text{Ni}(\text{Trien})^{2+}]_{\text{T}} = 2.5 \times 10^{-6} \text{ M}$ ;  $[\text{Par}]_{\text{T}} = 1.0 \times 10^{-4} \text{ M}$ ;  
 $I = 0.1$ , temp. =  $30^\circ\text{C}$ .

pH	$k_{\text{obsd}}$
6.7	$2.4 \times 10^{-4}$
7.2	$2.5 \times 10^{-4}$
7.7	$2.4 \times 10^{-4}$
8.1	$2.2 \times 10^{-4}$
8.4	$2.7 \times 10^{-4}$
8.6	$2.6 \times 10^{-4}$
8.9	$2.7 \times 10^{-4}$
9.2	$2.0 \times 10^{-4}$
9.7	$1.7 \times 10^{-4}$
10.4	$1.9 \times 10^{-4}$

#### V.7.2 Effect of Temperature

Activation parameters for both reaction steps were calculated using Arrhenius plots and are given in Table V.10

Table V.10. Effect of temperature on the reaction of  $\text{Ni}(\text{trien})^{2+}$  with Par at  $\text{pH}=9.0$ ,  $I=0.1\text{M}$ .

A. Formation of ternary complex $\text{Ni}(\text{trien})(\text{Par})$ .	B. Formation of $\text{Ni}(\text{Par})_2$ from $\text{Ni}(\text{trien})(\text{Par})$ .
$E_a = 14.1 \text{ kcal mol}^{-1}$	$E_a = 12.5 \text{ kcal mol}^{-1}$
$\Delta H^\ddagger = 13.5 \text{ kcal mol}^{-1}$	$\Delta H^\ddagger = 11.9 \text{ kcal mol}^{-1}$
$\Delta S^\ddagger = 6.5 \text{ e.u.}$	$\Delta S^\ddagger = -37.7 \text{ e.u.}$
$k_Z = 1.7 \times 10^{14} \text{ cm}^{-1}$	$k_Z = 4.12 \times 10^4 \text{ cm}^{-1}$

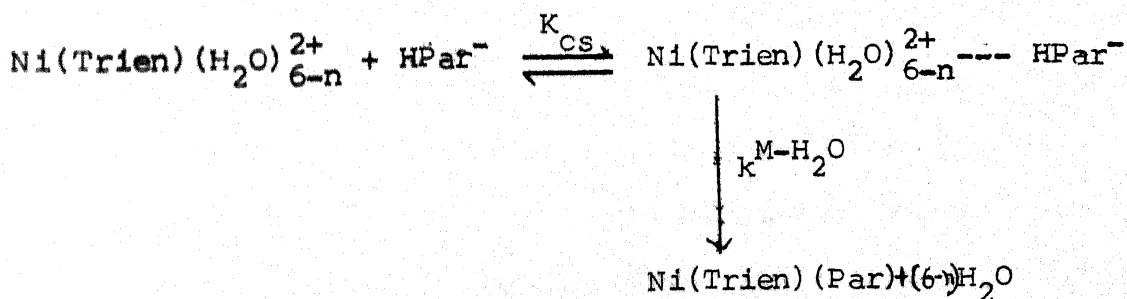
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## V.8 DISCUSSION

It is proposed that the ligand substitution reaction of metal-polyamine chelates with Par proceeds through the formation of a stable reaction intermediate in which the metal ion is bonded with both leaving and the incoming ligand. It has been shown<sup>14-16</sup> that a simple water loss mechanism via formation of an outer-sphere complex is operative during the formation of ternary complexes in many systems involving nickel as a central metal ion and the loss of first water molecule is the rate determining step. Tet and Trien are pentadentate and tetradentate respectively. The available coordination sites in the  $\text{NiTet}$  and  $\text{NiTrien}$  complexes are at least one and two respectively. The rate determining step ( $k_1$ ) of the first stage of the ligand substitution reactions reported here might be the loss of a

water molecule coordinated to the nickel complex. Par is a tridentate ligand being coordinated to nickel ion to form two five-membered chelate rings<sup>17</sup>. Therefore, it is reasonable to expect that there should be dissociation of at least two donor sites of coordinated ligand in the case of NiTet and one in the case of NiTrien complex before the incoming ligand can coordinate to the metal ion.

The kinetic behaviour of above said reaction (i.e. formation of ternary complexes) can be assumed to follow the general mechanism for metal-ligand complex formation as formulated by Eigen<sup>14-16</sup>. The nickel-polyamine complex ion and the entering ligand  $\text{HPar}^-$  are in rapid equilibrium with an outer sphere complex in which the entering group occupies a position in the coordination sphere and the rate determining step is the loss of a coordinated water molecule.



where  $K_{\text{os}}$  is the equilibrium constant for the outer sphere association,  $n$  is the number of bonding sites of polyamine and  $k^{M-\text{H}_2\text{O}}$  is the rate constant for rupture of polyamine nickel(II) complex-water bond.

The observed formation rate constant is then given by

$$k_{ML} = K_{OS} k^{M-H_2O} \quad \dots (16)$$

The value of the outer-sphere complex equilibrium constant  $K_{OS}$  depends on both the size and charge of the substituting ligand in accordance with the expression<sup>18-20</sup>

$$K_{OS} = \frac{4\pi N_A a^3}{3000} e^{-U(a)/kT} \quad \dots (17)$$

$$\text{where } U(a) = \frac{Z_A Z_B e^2}{a D} - \frac{Z_A Z_B e^2 \kappa}{D(1 + \kappa a)} \quad \dots (18)$$

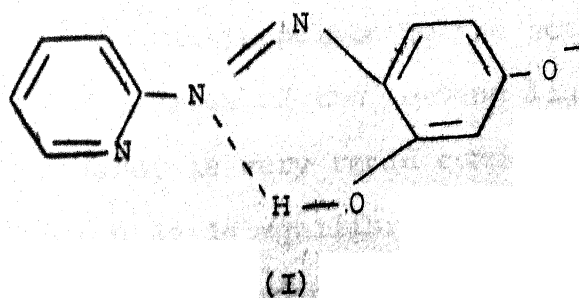
$$\text{and } \kappa = \left( \frac{8\pi N_A e^2}{1000 D kT} \right)^{1/2} \quad \dots (19)$$

In these equations  $N_A$  is the Avagadro's number, 'a' is the distance of closest approach of the two reacting ions (in cms),  $k$  is the Boltzmann constant (in ergs),  $T$  is the absolute temperature,  $e$  is the charge on an electron (in e.s.u),  $D$  is the bulk dielectric constant,  $I$  is the ionic strength and  $Z_A$  and  $Z_B$  are the charges on the metal complex and the ligand respectively. Various values of 'a' have been used by different investigators in the reaction systems studied by them. For example, Gordon et al.<sup>21</sup> have used values between  $3.5-5A^\circ$  for reaction of  $Ni(H_2O)_6^{2+}$  with some neutral ligands, while Cusumano<sup>22</sup> used a value of  $6A^\circ$  for complexation of nickel(II) in nonaqueous solvents with some azo dyes. We have made use of a value of  $6A^\circ$  based on reasonable



estimates. The values of water exchange rate for NiTrien and NiTet determined by Hunt et al.<sup>23</sup> are  $(5.7 \pm 1.6) \times 10^5 \text{ s}^{-1}$  and  $(112 \pm 22) \times 10^5 \text{ s}^{-1}$  per water molecule respectively. The values of rate constants calculated from equation (16) for the reactions of  $\text{NiTrien}^{2+}$  and  $\text{NiTet}^{2+}$  with  $\text{HR}^-$  are  $2.1 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$  and  $4.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$  respectively compared to the experimentally observed values of  $2.28 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$  and  $1.1 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$  for  $k_{\text{HR}}^{\text{NiTrien}}$  and  $k_{\text{HR}}^{\text{NiTet}}$  respectively (Table V.8).

Par contains a pyridine ring and a phenolic ring and may well exert steric effects on the complexation process. A situation may also arise where the ring closure makes a sufficient contribution towards the rate determining step. This situation was first observed in the reactions of Ni(II) and Co(II) with  $\beta$ -alanine in water<sup>24,25</sup>. The lower values of  $k_{\text{HR}}^{\text{Nip}}$  for reaction of Ni(II) complexes with Par compared to that of water exchange per molecule can be interpreted by assuming that these reactions are sterically controlled. This assumption is supported by the fact that ring closure implies breaking of the strong intra molecular hydrogen bond<sup>26-28</sup> between the orthophenolic proton and the azo-nitrogen(I).



The activation enthalpies are 11 kcal and 13.5 kcal for Ni(Trien) and Ni(Tet) reactions respectively. They are comparable to  $\Delta H^\ddagger$  for water exchange at nickel(II) for which several values have been quoted but two typical values are  $12.1 \pm 0.5^{29}$  and  $13.8^{30}$  kcal mol<sup>-1</sup>. These are also comparable with values for the reaction of 5-nitrosalicylic acid with NiTrien and NiDien for which  $\Delta H^\ddagger$  are  $11.3^{31}$  and  $12.5 \pm 1.5^{32}$  kcal mol<sup>-1</sup> respectively. Also, the  $\Delta S^\ddagger$  is slightly positive reflecting the greater desolvation associated with the charge neutralisation which occurs during formation of transition state between two charged ions, viz. NiTrien<sup>2+</sup> or NiTet<sup>2-</sup> and HR<sup>-</sup> than between nickel complex and neutral incoming ligands.

The second stage of reaction involves the formation of Ni(Par)<sub>2</sub> accompanied by dissociation of ternary complex, Ni(Polyamine)(Par). The experimental data for this reaction show that the rate determining step for this stage involves dissociation of polyamine prior to the addition of second molecule of Par, because no dependence on Par has been observed for this stage.

The increase in rate of dissociation of polyamine for the second step of ligand substitution process in case of the (NiTet)<sup>2+</sup> complex with decreasing pH points to the active role of protons in assisting dissociation of the leaving ligand in the complex. Since proton transfer is very rapid compared to other reaction steps<sup>19</sup>, the proton is in equilibrium with the protonated intermediate Ni(HTet)(Par) preceding the rate determining step. The

proton bound to the leaving group facilitates the dissociation of the leaving group as observed for ligand substitution reactions of NiTrien with Phen<sup>11</sup> in the pH range 5-6.8. The dissociation of Trien in Ni(Trien)(Par) was studied between pH 7-10.6 and it was found that the dissociation rate remains almost unaffected by change in hydrogen ion concentration. This may be due to the fact that in this pH range, the reactive species of Ni(Trien) complex are Ni(Trien) and NiTrien(OH) which on reaction with Par give Ni(Trien)(Par) and no proton is involved in its dissociation followed by reaction with HPar<sup>-</sup> to give Ni(Par)<sub>2</sub> as the final product.

The values of  $\Delta S^\ddagger$  for the first stage of reaction are slightly positive but for the second stage are highly negative (Table V.2&V.10). Tet and Trien are pentadentate and quadridentate respectively while Par is tridentate. During formation of the ternary complex Ni(Polyamine)(Par) some binding site of polyamine would remain uncomplexed causing some increase of disorder accompanied by small increase in entropy. During the second stage, however, the partly chelated ligand viz. polyamine dissociates completely during the formation of activated complex to give a more orderly octahedral configuration NiR.3H<sub>2</sub>O accounting for the large decrease in entropy reported in Table V.2 & V.10.

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The reverse reaction between  $\text{Fe}(\text{CN})_5(\text{OH})^{3-}$  and EDTA shows an inverse first order dependence in cyanide along with first order dependence each in  $\text{Fe}(\text{CN})_5(\text{OH})^{3-}$  and EDTA. A five step mechanism is proposed for the first reaction which is consistent with all the experimental observations. The second and third reactions are also examined at some length.

## VI.1 INTRODUCTION

The substitution of multidentate ligands in their complexes of metal ions by monodentate ligands has evoked the interest of many workers. The polyaminocarboxylates of  $\text{Ni}(\text{II})^1$ ,  $\text{Co}(\text{II})^{2,3}$  and  $\text{Mn}(\text{III})^4$  have received attention for their exchange reactions with a potential monodentate cyanide ion as an incoming ligand. Results of studies on substitution reactions of  $\text{Fe}(\text{II})$  complexes of 1,10 phenanthroline<sup>5,6</sup> and 2,2' bipyridyl<sup>7</sup> with cyanide ion are also available. However, no investigation has so far been reported about the reaction of aminocarboxylato complexes of  $\text{Fe}(\text{III})$  with cyanide ion.\*

In this investigation the kinetics and mechanism of the reaction of cyanide ion with ethylenediaminetetraacetato-ferrate(III) complex is reported which may lead to a better understanding of the interaction of biologically important  $\text{Fe}(\text{III})$  complexes with the highly toxic cyanide ion.

The EDTA complex of  $\text{Fe}(\text{III})$  ( $\text{FeY}$ ,  $\text{Y}=\text{EDTA}$ ) is believed to be a seven coordinated species having one water molecule in the

solid state as well as in neutral or acidic media<sup>8</sup>. In presence of a base it loses a proton to give a hydroxo species  $\text{FeY}(\text{OH})^8$  which is reported to be a stable species in the pH range higher than 9.

## VI.2 EXPERIMENTAL

Disodium salt of ethylenediaminetetraacetic acid AR(BDH), Ferric Nitrate (Thomas & Baker), Sodium cyanide M & B Ltd (England), Sodium perchlorate E. Merck (Germany) and Sodium ferricyanide GR (SDS) were used for this study. Pentacyano(aquo) ferrate(III) was prepared from sodium nitroprusside AR(BDH) by a method described in literature<sup>9</sup>. On passing ammonia, under specified conditions pentacyano(ammino)ferrate(II) crystallised out. On dissolution in water, ammonia was replaced resulting in the formation of pentacyano(aquo)ferrate(II). This was oxidised to pentacyano(aquo)ferrate(III) using hydrogen peroxide<sup>10</sup> and then used for the study of reverse reaction.

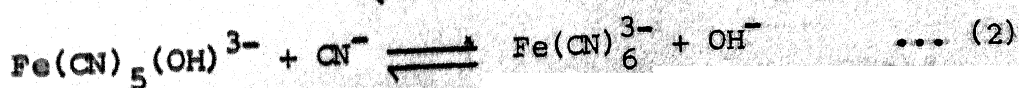
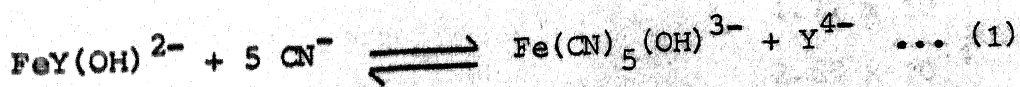
Ferric perchlorate was prepared by dissolution of a precipitate of  $\text{Fe}(\text{OH})_3$  in calculated quantity of perchloric acid. Ferric perchlorate thus prepared was standardised complexometrically using sulphosalicyclic acid as an indicator and used for preparation of  $\text{FeY}(\text{H}_2\text{O})$  complex. To ensure complete formation of  $\text{FeY}(\text{H}_2\text{O})$  an amount of EDTA 10% in excess of stoichiometric requirement was mixed with ferric perchlorate. Sodium cyanide was standardised argentometrically<sup>12</sup>. Perchloric acid or sodium

### VI.2.1 Apparatus

A Toshniwal Spectrophotometer Model RL-02 attached with a circulatory arrangement for thermostating the cell compartment was used for kinetic study of this reaction. An ultracryostat model 2NBE (GRD) was used for maintenance of desired temperature within  $\pm 0.1^\circ\text{C}$ , Cary 17 D spectrophotometer was used for time scanning of the reaction. All pH measurements were made on an Elico Digital pH meter (Model LI-120) using BDH standard buffer solutions for standardization.

### VI.3 KINETIC MEASUREMENTS

The exchange reaction of  $\text{FeY(OH)}^{2-}$  with cyanide was followed at 395 nm ( $\lambda_{\text{max}}$  of  $\text{Fe(CN)}_5\text{OH}^{3-}$ ,  $\epsilon = 1740 \text{ M}^{-1}$ )<sup>13</sup> at pH = 10.5,  $I = 0.25 \text{ M}(\text{NaClO}_4)$  and temp. =  $25^\circ\text{C}$ . The exchange reactions were run in presence of sufficiently large excess of the incoming ligand viz. cyanide. The pseudo first order rate constants were calculated from plots of  $\ln(A_\infty - A_t)$  vs  $t$ , over 70% of the reaction. The  $A_\infty$  value used for pseudo first order plots was a theoretically calculated one supposing that the reaction goes to completion for the formation of  $\text{Fe(CN)}_5\text{OH}^{3-}$ . This had to be done because after a certain concentration of  $\text{Fe(CN)}_5\text{OH}^{3-}$  builds-up according to equation (1), the same is converted to  $\text{Fe(CN)}_6^{3-}$  according to equation (2).





The reverse reaction was followed at 395 nm ( $\lambda_{\text{max}}$  of  $\text{Fe}(\text{CN})_5(\text{OH})^{3-}$ ) taking  $\text{Fe}(\text{CN})_5(\text{OH})$  and excess EDTA as reactants.

#### VI.4 RESULTS

The  $\text{FeY}(\text{H}_2\text{O})^-$  prepared by adding 10% excess of EDTA to  $\text{Fe}(\text{III})$  is present as  $\text{FeY}(\text{OH})^{2-}$  at a pH higher than 9. Under pseudo first order conditions and at pH = 10.5 the reaction was found to be first order with respect to metal complex and exhibits a variable order with respect to cyanide. The pseudo first order rate constants at various cyanide concentrations are given in Table VI.1. A plot of  $\log k_{\text{obsd}}$  vs  $\log [\text{CN}^-]_T$  (Fig. VI.1) shows a variable order

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Table VI.1. Cyanide Dependence of the observed pseudo first order rate constants for the reaction of cyanide ion with  $\text{FeY}(\text{OH})$ .

$[\text{FeY}(\text{OH})]_T^{2-} = (3-6) \times 10^{-4} \text{ M}$ , pH = 10.5, temp. = 25°C,  
 $i = 0.25 \text{ M } (\text{NaClO}_4)$

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$10^2 \times [\text{CN}^-]_T, \text{ M}$	$k_{\text{obsd}}, \text{ sec}^{-1}$
2.5	$1.62 \times 10^{-5}$
3.5	$5.25 \times 10^{-5}$
4.4	$1.02 \times 10^{-4}$
5.0	$1.72 \times 10^{-4}$
6.5	$2.65 \times 10^{-4}$

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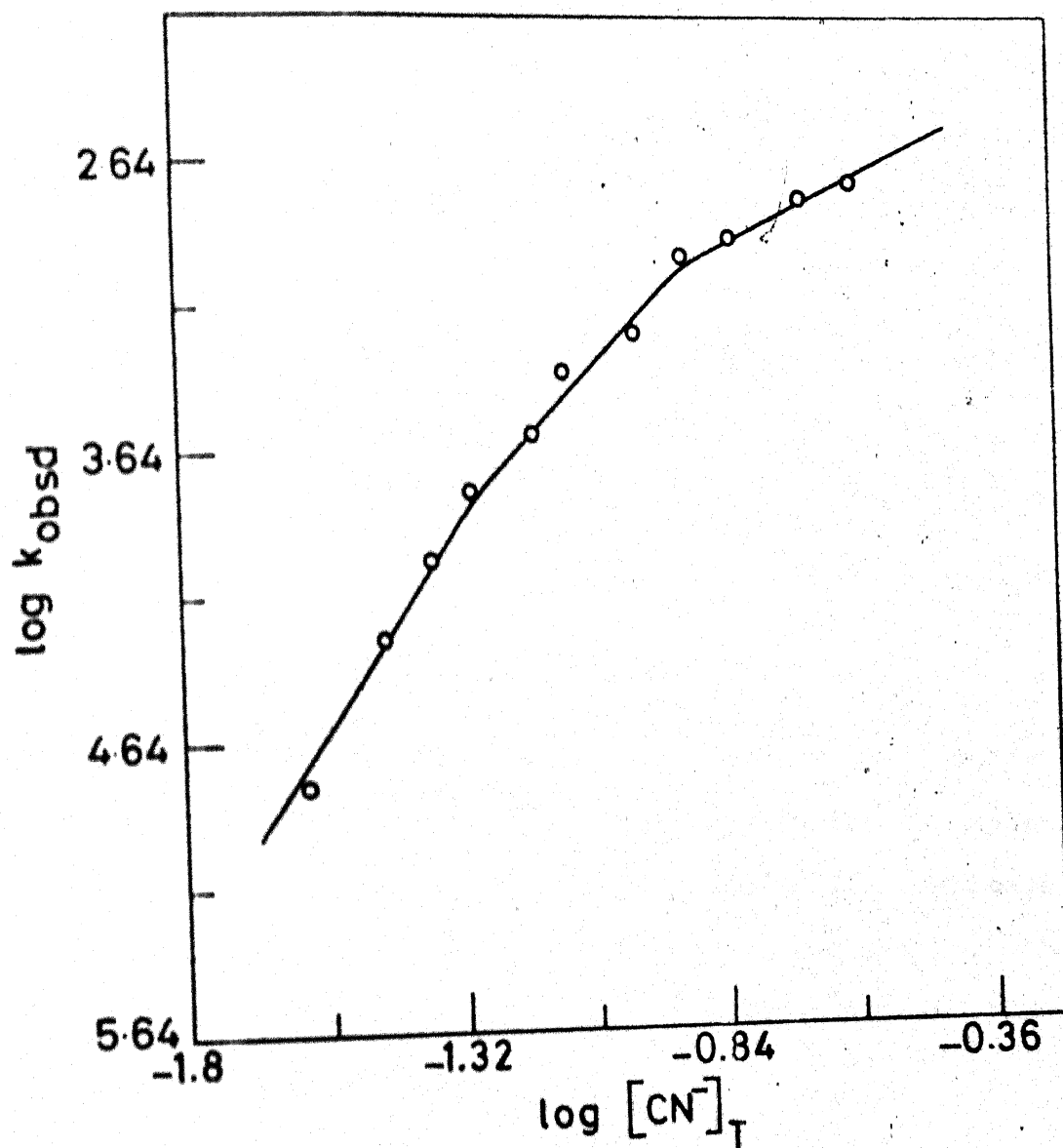


Fig. VI.1 Cyanide dependence of the observed Pseudo first order rate constants in the reaction of cyanide ion with  $\text{Fe}(\text{EDTA})\text{OH}$ ;  
 $[\text{Fe}(\text{EDTA})\text{OH}] = (3-6) \times 10^{-4} \text{ M}$ ;  $\text{pH} = 10.5$ ,  $\text{temp.} = 25^\circ\text{C}$   
 and  $I = 0.25 \text{ M}$  ( $\text{NaClO}_4$ ).

7.5	$4.26 \times 10^{-4}$
10.0	$5.94 \times 10^{-4}$
12.5	$1.10 \times 10^{-3}$
15.0	$1.26 \times 10^{-3}$
20.0	$1.74 \times 10^{-3}$
25.0	$1.93 \times 10^{-3}$

---

in cyanide varying from one at high concentration to three at low cyanide concentration. This result points to a step-wise displacement of EDTA by cyanide ions. Similar observations for stepwise displacement of outgoing ligand were also made by Margerum et al.<sup>1</sup> and Nakamura<sup>2</sup> while studying the exchange of some aminocarboxylates on their Ni(II) and Co(II) complexes by cyanide ion, and by Nigam et al.<sup>4</sup> later for exchange of other polyaminocarboxylates of Ni(II) with cyanide ion.

#### VI.5 Dependence of Forward Rate on pH:

The forward reaction was studied in the pH range 9-11 and the rate was found to increase with an increase of pH (Table VI.2). This increase in rate constant cannot be accounted for by difference in reactivities of  $\text{CN}^-$  and HCN alone as reactive nucleophiles. Neither is it possible to resolve rate constants  $k_{\text{HCN}}$  and  $k_{\text{CN}^-}$  for the two reactants because of the complexity

Table VI.2. Effect of  $H^+$  ion concentration on the reaction of  $FeY(OH)^{2-}$  and cyanide ion to form  $Fe(CN)_5(OH)^{3-}$ .

$[FeY(OH)^{2-}]_T = 5 \times 10^{-4} M$ ,  $[CN^-]_T = 0.22 M$ ,  
 $I = 0.25 M$  ( $NaClO_4$ ), temp. =  $25^\circ C$ .

pH	$k_{obsd}, s^{-1}$
9.3	$5.7 \times 10^{-6}$
9.6	$3.7 \times 10^{-5}$
9.9	$8.9 \times 10^{-5}$
10.1	$1.97 \times 10^{-4}$
10.4	$4.6 \times 10^{-4}$
10.7	$1.25 \times 10^{-3}$
11.0	$1.78 \times 10^{-3}$

arising out of subsequent reactions involving the conversion of  $Fe(CN)_5(OH)^{3-}$  to  $Fe(CN)_6^{3-}$  and the reduction of latter to  $Fe(CN)_6^{4-}$  which is highly  $[OH^-]$  dependent.

#### VI.6 The Kinetics of Reverse Reaction:

The reverse reaction was studied taking  $Fe(CN)_5(OH)^{3-}$  as a reactant. A large excess of EDTA had to be used to drive the reaction and the reaction rate was found to be very slow. This is not unexpected because the estimated value of stability constant for  $Fe(CN)_5(OH)^{3-}$  is much higher than the stability constant

of  $\text{FeY(OH)}$  ( $\log \beta_{\text{FeY(OH)}} = 31.0^{15}$ ). Although the stability constant of the former is not known, it is expected to be smaller than the  $\beta_6$  of  $\text{Fe(CN)}_6^{3-}$  ( $\log \beta_6 = 43.2^{16}$ ) but not too small. Further, the reaction of  $\text{Fe(CN)}_5\text{(OH)}^{3-}$  with EDTA was found to be first order each with respect to EDTA and  $\text{Fe(CN)}_5\text{OH}^{3-}$  and showed inverse first order dependence in cyanide. The following integrated rate equation (3) which reflects inverse first order dependence in cyanide, was used to calculate the reverse rate constants

$$(A_1 - A_t) + A_1 \ln \frac{A_t}{A_1} = - \frac{\epsilon l}{5} k'_{\text{obsd}} \cdot t \quad \dots (3)$$

where  $A_1$  = initial absorbance,  $A_t$  = Absorbance at time  $t$ ,  
 $\epsilon$  = Molar extinction coefficient of  $\text{Fe(CN)}_5\text{OH}^{3-}$  at 395 nm,  
 $k'_{\text{obsd}} = k_r [Y^{4-}]$  and  $Y = \text{EDTA}$ .

The rate constants obtained from the plots of the left hand side of equation (3) vs  $t$  are given in Table VI.3..

Table VI.3. Kinetics of reaction between  $\text{Fe(CN)}_5\text{OH}$  and EDTA

$[\text{Fe(CN)}_5\text{OH}^{3-}]_T = 5 \times 10^{-4}$ ,  $[\text{EDTA}]_T = 0.1\text{M}-0.5\text{M}$ ,  
 $\text{pH} = 10.5$ ,  $I = 0.5\text{M}$ ,  $\text{temp.} = 30^\circ\text{C}$ .

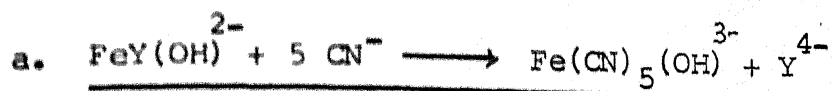
$[\text{EDTA}^{4-}]_T, \text{M}$	$10^7 \times k'_{\text{obsd}}, \text{sec}^{-1}$	$10^6 \times k_r (=K_5^{-1} k_{-4}), \text{sec}^{-1}$
0.1	1.5	1.5
0.25	3.6	1.44
0.4	6.1	1.52
0.5	7.1	1.42
$\text{Av}(1.47 \pm .05) \times 10^{-6}, \text{sec}^{-1}$		

A few kinetic runs were also taken for the reaction between  $\text{Fe}(\text{CN})_6^{3-}$  and EDTA taken in large excess, contrary to expectation based on the criteria of stability constants, ( $\log \beta_6 = 43.6^{16}$  for  $\text{Fe}(\text{CN})_6^{3-}$ ,  $\log \beta_{\text{FeY}(\text{OH})^{3-}}^{15}$ ), the rate of this reaction is quite fast. It was also found that the rate is first order in  $\text{Fe}(\text{CN})_6^{3-}$  and first order in EDTA, second order over all. The rate constants calculated on this basis, from a few kinetic runs, are given later in Table VI.5. This reaction was not pursued further because the reaction is mainly a redox reaction rather than a substitution one. The products of this reaction according to an earlier study<sup>17</sup> are  $\text{Fe}(\text{CN})_6^{4-}$  and the oxidation products of EDTA.

#### VI.7 Effect of temperature on different reactions occurring in the system:

Activation parameters have been calculated from the Arrhenius plots in the temperature range 25-40°C for the reaction between  $\text{FeY}(\text{OH})^{2-}$  and cyanide ion and have also been calculated for the reaction between  $\text{Fe}(\text{CN})_5(\text{OH})^{3-}$  and cyanide ion. These are given in Table VI.4. Activation parameters for the oxidation reduction reaction between  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{Y}^{4-}$  based on an earlier study<sup>17</sup> have been included in Table VI.4 for the sake of completeness.

Table VI.4. Activation parameters for different reactions occurring in the whole reaction system *per mole*,

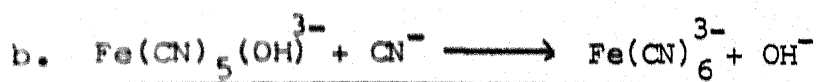


$E_a = 10.7 \text{ kcal}$

$\Delta H^\ddagger = 10.1 \text{ kcal}$

$\Delta S^\ddagger = -32.3 \text{ e.u.}$

$pZ = 5.8 \times 10^5 \text{ cm}^{-1}$

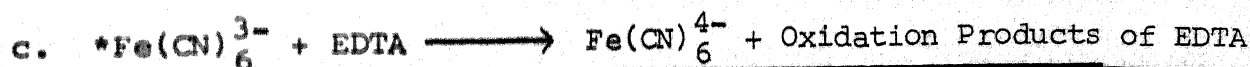


$E_a = 7.3 \text{ kcal}$

$\Delta H^\ddagger = 6.7 \text{ kcal}$

$\Delta S^\ddagger = -52.4 \text{ e.u.}$

$pZ = 2.6 \times 10^1 \text{ cm}^{-1}$



$E_a = 17.2 \text{ kcal}$

$\Delta H^\ddagger = 16.6 \text{ kcal}$

$\Delta S^\ddagger = 6.8 \text{ e.u.}$

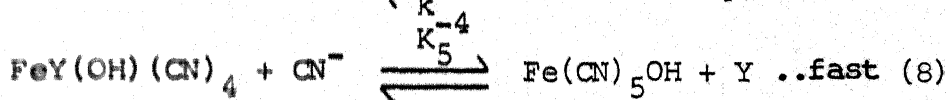
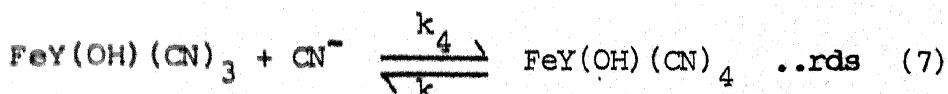
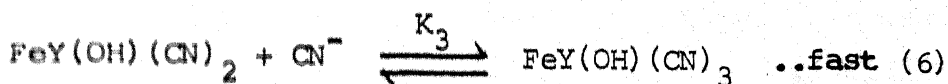
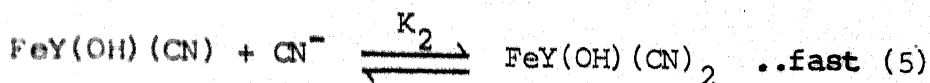
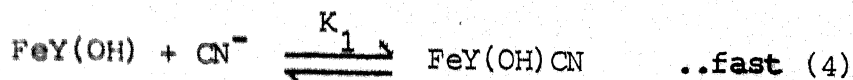
$pZ = 1.9 \times 10^{14} \text{ cm}^{-1}$

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\* From Ref. (17).

## VI.8 DISCUSSION

The experimental observations and analysis of data for forward and backward reactions are compatible with the mechanism given below from equations 4-8 (charges have been omitted for sake of clarity).



The inverse first order dependence in cyanide for the reverse reaction, when  $\text{Fe(CN)}_5\text{OH}^{3-}$  is the reactant, enables one to pinpoint the rate determining step as the fourth one (equation 7). The variable order dependence in cyanide for the forward reaction which changes from one to three coupled with the above observation leads to the proposition that the first step is very fast and a 1:1:1  $\text{FeY(OH)CN}$  intermediate is formed instantaneously and the same is sufficiently stable also. Similar proposition for the rapid formation of 1:1:1 hepta coordinated intermediates was also envisaged by Margerum<sup>3</sup> and Hamm et al.<sup>4</sup> while studying the exchange of CyDTA on  $\text{Co(II)CyDTA}$  and  $\text{Mn(III)-CyDTA}$  complexes with  $\text{CN}^-$ . The rate of complete replacement of EDTA by cyanide



to give  $\text{Fe}(\text{CN})_5\text{OH}^{3-}$  is slow. Three cyanides react with this intermediate (obtained in equation 4) to produce  $\text{FeY}(\text{CN})_4(\text{OH})$  in the rate determining step, giving rise to the observed third order dependence in cyanide at low cyanide concentrations. As the concentration of cyanide increases, the reactants become  $\text{FeY}(\text{CN})_2\text{OH}$  or  $\text{FeY}(\text{CN})_3\text{OH}$ , which accounts for the observed second and first order dependences in cyanide respectively. A fourth order dependence could be observed if the reactant was  $\text{FeY}(\text{OH})$  and not  $\text{FeY}(\text{OH})\text{CN}$  as proposed. We failed to see this because at still lower concentrations of cyanide where  $\text{FeY}(\text{OH})$  may become a reactant, the reaction rate becomes too slow for dependable measurements.

In Fig VI.2 two typical plots of  $\log(A_\infty - A_t)$  vs  $t$  under pseudo first order conditions ( $[\text{cyanide}] = .025\text{M}$  and  $0.15\text{M}$ ,  $[\text{FeY}(\text{OH})] = 5 \times 10^{-4}\text{M}$ ,  $I = 0.5\text{M}$  ( $\text{NaClO}_4$ ),  $\text{temp.} = 25^\circ\text{C}$  and  $\text{pH} = 10.5$ ) followed at 395 nm are shown. Distinct deviations from linearity were observed at various cyanide concentrations. Interestingly the deviations in pseudo first order plots were found to be negative in case of low cyanide and positive at high cyanide concentrations. This observation led to the conclusion that these deviations are not due to reversibility but are due to the fact that some other reaction involving cyanide is also going on in the system. The chances of reversibility seem to be remote due to higher stability of cyano complexes and large excess of cyanide present in the system.

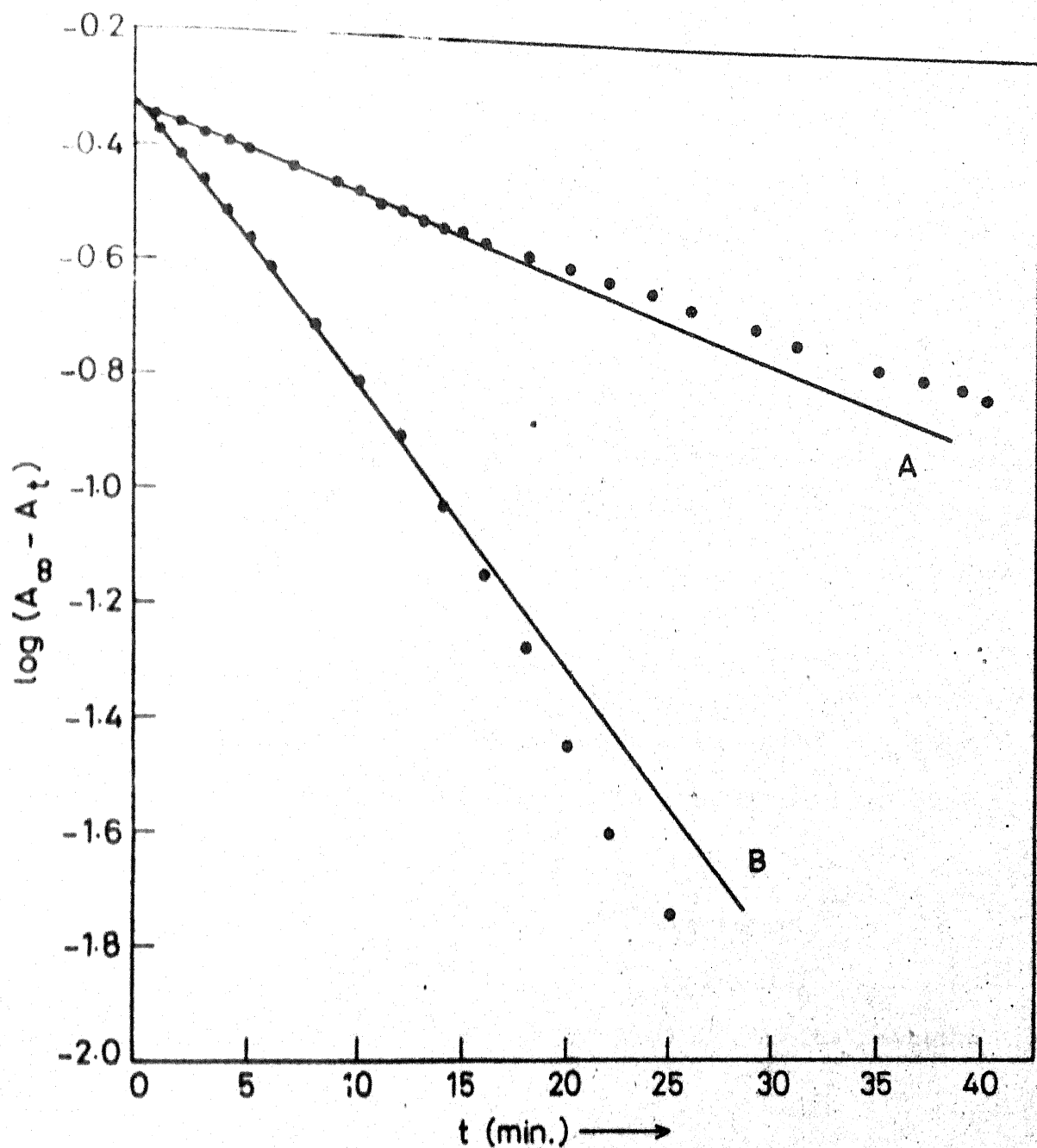


Fig. VI.2 Pseudo first order plots for the reaction of  $\text{Fe(EDTA)OH}$  with cyanide ion.

$[\text{Fe(EDTA)OH}] = 5 \times 10^{-4} \text{ M}$ ,  $\text{pH} = 10.5$ ,  $\text{temp.} = 25^\circ\text{C}$  and  $I = 0.25 \text{ M}$  ( $\text{NaClO}_4$ ).

(A)  $[\text{CN}^-]_{\text{T}} = 0.075 \text{ M}$ , (B)  $[\text{CN}^-]_{\text{T}} = 0.2 \text{ M}$ .

The time scan of this reaction on Cary 17D is shown in Fig. VI.3. From this figure it is clear that there is a continuous increase in the peak height of  $\text{Fe}(\text{CN})_5\text{OH}^{3-}$  (395 nm) in the beginning of reaction but when sufficiently high concentration of ( $\sim 95\%$  of theoretical value) pentacyanohydroxoferrate(III) is built up the same starts converting to  $\text{Fe}(\text{CN})_6^{3-}$ . The lowering of peak at 395 nm with a shift towards 410-420 nm ( $\lambda_{\text{max}}$  region of  $\text{Fe}(\text{CN})_6^{3-}$ ) region confirms this inference. Finally, there is a decrease in height of this peak also and with time all peaks in visible region of spectrum almost vanish.

These observations lead to the conclusion that  $\text{Fe}(\text{CN})_5\text{OH}^{3-}$  is not the final product of this reaction and that the total reaction of  $\text{FeY}(\text{OH})$  with excess cyanide can be divided into 3 distinguishable parts

- (a) Formation of  $\text{Fe}(\text{CN})_5(\text{OH})^{3-}$  from  $\text{FeY}(\text{OH})^{2-}$
- (b) Conversion of  $\text{Fe}(\text{CN})_5(\text{OH})^{3-}$  to  $\text{Fe}(\text{CN})_6^{3-}$
- (c) Reduction of  $\text{Fe}(\text{CN})_6^{3-}$  to  $\text{Fe}(\text{CN})_6^{4-}$  due to reaction with EDTA.

The appearance of three isosbestic points (Fig. VI.3) in time scan spectra during course of reaction also confirms that the above said reactions are taking place at different stages of progress of reaction. The first isosbestic point at 350 nm indicates the equilibrium between  $\text{FeY}(\text{OH})$  and  $\text{Fe}(\text{CN})_5\text{OH}^{3-}$ . The second stage of reaction is the conversion of  $\text{Fe}(\text{CN})_5\text{OH}^{3-}$  to  $\text{Fe}(\text{CN})_6^{3-}$  which is distinct from the first stage and the appearance

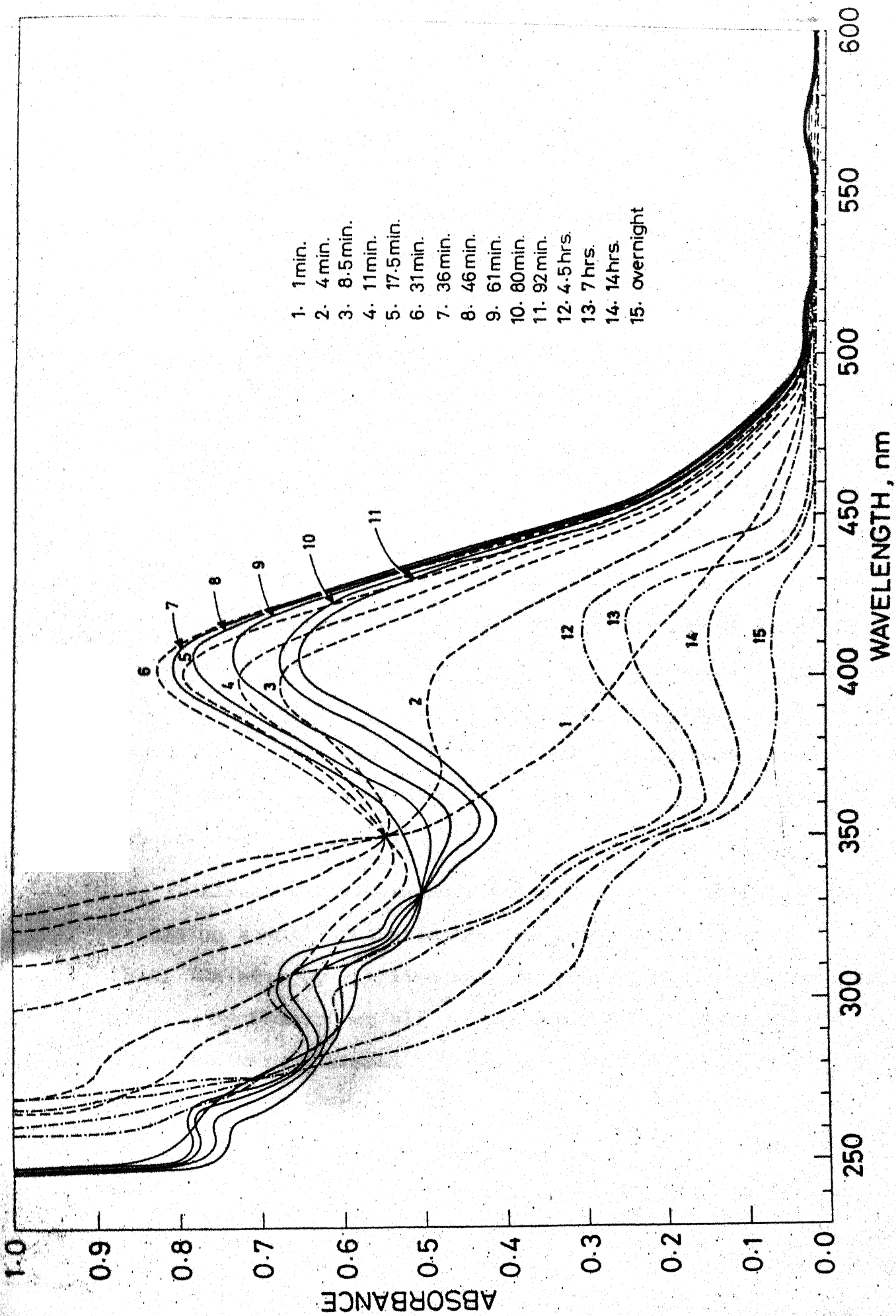


Fig. VI-3 Rapid scan of the reaction mixture during a typical kinetic run at 30°C,  $[\text{Fe}(\text{EDTA})\text{OH}] = 5 \times 10^{-5} \text{ M}$ ,  $[\text{CN}^-] = 0.15 \text{ M}$ ,  $\text{pH} = 10.5$ ,  $I = 0.25 \text{ M}$  ( $\text{NaClO}_4$ )

of a second isosbestic point at 330 nm indicates an equilibrium between these two species. Two new peaks at 257 and 309 nm also show the formation of  $\text{Fe}(\text{CN})_6^{3-18}$  at the same time. It is interesting that a new low absorption band appears in later stage of reaction in 510-570 nm region. This is due to formation of  $\text{Fe}_2(\text{CN})_{10}$  ( $\lambda_{\text{max}}$  of  $\text{Fe}_2(\text{CN})_{10} = 568 \text{ nm}$ ;  $\epsilon = 1600 \text{ M}^{-1} \cdot \text{cm}^{-1}$ ) in very small concentration due to dimerisation of  $\text{Fe}(\text{CN})_5\text{OH}^{3-}$ . A scan of this same region at higher sensitivity of the instrument showed a small but not insignificant increase in absorption due to the formation of the dimer. This also decays, however, due to ultimate conversion into  $\text{Fe}(\text{CN})_6^{3-}$ .

The spectroscopic evidence for reduction of  $\text{Fe}(\text{CN})_6^{3-}$  to  $\text{Fe}(\text{CN})_6^{4-}$  is provided by presence of a third new isosbestic at 276 nm. There is a continual decrease of absorbance at 304 nm region ( $\lambda_{\text{max}}$  of  $\text{Fe}(\text{CN})_6^{3-}$ )<sup>18</sup> along with a matching increase in absorbance at wavelength below 276 nm ( $\lambda_{\text{max}}$  of  $\text{Fe}(\text{CN})_6^{4-}$  at 265 nm,  $\log \epsilon = 2.3$ )<sup>18</sup>.

Alkaline hexacyanoferrate(III) is known to be a potential oxidising agent<sup>20</sup> and oxidation of some chelating agents like EDTA, IDA etc. by alkaline hexacyanoferrate(III) has been reported earlier by Lambert et al.<sup>17</sup>. The products of oxidation-reduction reactions were analysed by them and shown to be  $\text{Fe}(\text{CN})_6^{4-}$ , IDA and glycollic acid in case of EDTA. They also reported that the presence of cyanide increases the oxidation rate. 4 moles of  $\text{Fe}(\text{CN})_6^{3-}$  are used per mole of EDTA in this reaction. In our

system a 10% excess of EDTA over stoichiometric amount has been taken to ensure complete formation of  $\text{FeY(OH)}$  complex. Thus the whole of EDTA can not be oxidised even if all  $\text{Fe(CN)}_6^{3-}$  is used up in the reaction. A positive qualitative test for the presence of  $\text{Fe(CN)}_6^{4-}$  (ammonium molybdate test<sup>21</sup>) at the end and a negative test in the beginning of reaction confirms that the oxidation of EDTA by ferricyanide formed during the second stage of reaction does take place. The quantitative estimation of  $\text{Fe(CN)}_6^{4-}$  in presence of  $\text{Fe(CN)}_6^{3-}$  was done by titration with ceric ammonium-sulphate using Ferroin but consumption of  $\text{Ce(IV)}$  was always found to be higher than the expected value. This appears to be due to oxidation of the remaining unconsumed EDTA and IDA (which is one of the products of  $\text{Fe(CN)}_6^{3-}$  - EDTA reaction) by  $\text{Ce(IV)}$ <sup>21</sup>. This consumption is less at a time when no ferrocyanide is formed in the system.

The rate constants for the three different stages of the reaction are given in Table VI.5. The higher rate of reaction of EDTA with  $\text{Fe(CN)}_6^{3-}$  as the starting reactant may be due to much greater extent of oxidation reaction compared to the substitution reaction.

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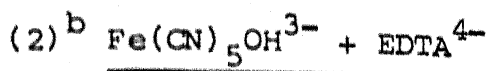
Table VI.5. Rate constants for various stages of reaction

(1) <sup>a</sup>  $\text{FeY(OH)}^{2-} + \text{CN}^-$

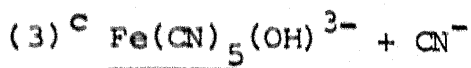
$$k_4 = 8.17 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

$$k_3 k_4 = 6.6 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$$

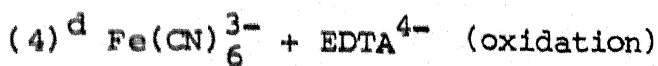
$$k_2 k_3 k_4 = 1.2 \times 10^0 \text{ M}^{-3} \text{ s}^{-1}$$



$$K_5^{-1} k_{-4} = (1.46 \pm .07) \times 10^{-6} \text{ s}^{-1}$$



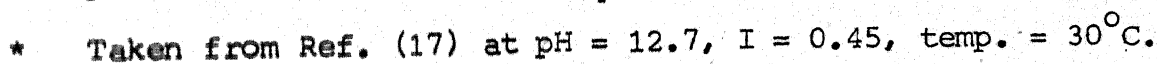
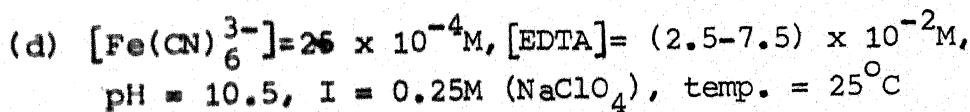
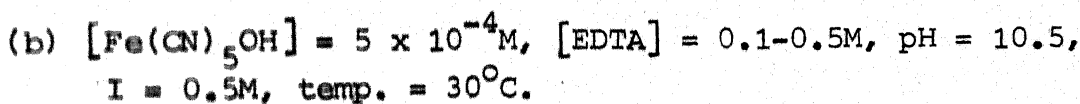
$$3.83 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$$



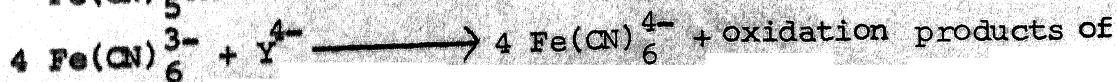
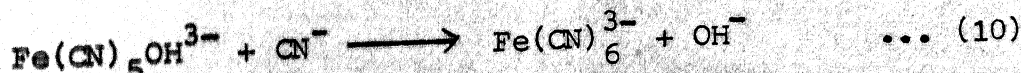
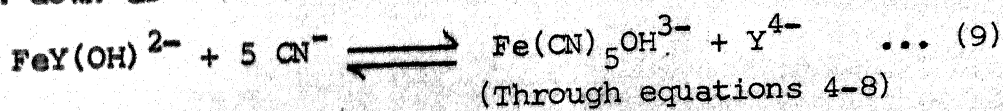
$$4.8 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$$

$$1.05 \times 10^{-1} \text{ M}^{-1}\text{s}^{-1*}$$

### Experimental conditions



Finally the sequence of three stages of reaction may be written down as



To the best of our knowledge this is the first detailed report on a ligand exchange process in an aminocarboxylate complex of iron(III) involving reaction with cyanide ions.





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## CHAPTER VII

### SUMMARY OF WORK AND SUGGESTIONS FOR FURTHER INVESTIGATIONS

#### VII.1 SUMMARY

The first chapter of the thesis presents a brief survey of the ligand substitution reactions of metal complexes in general and nickel(II) complexes in particular. Some space is devoted to the formation of ternary chelates and to the role of solvents in substitution reactions.

The second chapter deals with the reaction of a binuclear nickel(II) chelate,  $\text{Ni}_2\text{EGTA}$ , with cyanide ion. Kinetic results show that the reaction proceeds by two paths: a cyanide independent path at  $[\text{CN}^-]$  below  $10^{-3}\text{M}$ , in which the binuclear complex dissociates to  $\text{NiL}$  and  $\text{Ni}^{2+}_{(\text{aquo})}$ , and a cyanide assisted dissociation of  $\text{Ni}_2\text{L}$  finally leading to the formation  $\text{Ni}(\text{CN})_4^{2-}$  in both cases.

Chapter three deals with the reaction of two bis complexes of nickel(II),  $\text{NiL}_2$ , with cyanide ion, where L is dien and en. A slow self dissociation of  $\text{NiL}_2$  to  $\text{NiL}$  and L and a cyanide assisted dissociation of  $\text{NiL}_2$  to give  $\text{NiL}(\text{CN})_x$  and finally  $\text{Ni}(\text{CN})_4^{2-}$  has been established.

The fourth chapter of the thesis includes results on investigations of the reaction of HEEDTA and DTPA with  $\text{Ni}(\text{Trien})^{2+}$  resulting in the formation of  $\text{NiHEEDTA}^{1-}$  and  $\text{NiDTPA}^{3-}$  respectively. A stepwise unwrapping of trien and successive formation of amino-carboxylate bonds with nickel is involved. The effect of temperature and pH is also investigated and used to elucidate the mechanism.

The fifth chapter deals with the formation of  $\text{Ni}(\text{Par})_2$  (Par = 4(2-pyridylazo)resorcinol) from  $\text{Ni}(\text{Trien})^{2+}$  and  $\text{Ni}(\text{Tet})^{2+}$ . An interesting feature of these reactions is the formation of stable ternary mixed ligand complexes,  $\text{Ni}(\text{Polyamine})(\text{Par})$ , which undergo slow unwrapping of polyamine and give  $\text{Ni}(\text{Par})_2$ . The effect of pH and temperature on the formation and dissociation of mixed ligand complexes has also been discussed.

The sixth chapter describes the reaction of ethylenediaminetetraacetato(hydroxo)ferrate(III) with cyanide ion. This reaction appears to be quite complicated. The interesting feature of the reaction is the conversion of  $\text{FeY}(\text{OH})^{2-}$  to  $\text{Fe}(\text{CN})_6^{4-}$  via a three stage consecutive reaction sequence in which  $\text{FeY}(\text{OH})^{2-}$  is first converted in a five step process to  $\text{Fe}(\text{CN})_5(\text{OH})^{3-}$ , then to  $\text{Fe}(\text{CN})_6^{3-}$  and finally to  $\text{Fe}(\text{CN})_6^{4-}$ . Rate constants for all the steps have been reported.

The present and the last chapter give a summary of the whole thesis and suggestions for the further work which are discussed now onwards.

## VII.2 Suggestions for the further work

It is felt that the investigations can be extended to many new system some of which are enumerated below:

- I. To study the reaction of  $\text{CN}^-$  ion with some binuclear nickel(II) chelates such as  $\text{Ni}_2\text{TPHA}$  (where TPHA is tetraethylene-pentaamineheptaacetic acid) in order to elicit further support for the mechanism proposed herein.
- II. To study the reaction of  $\text{CN}^-$  ion with mono and binuclear nickel(II) complexes of biologically important macromolecules.
- III. To study the kinetics of exchange reactions of some bis complexes of nickel(II) and polyamines with other multidentate ligands.
- IV. To study the reaction of some binuclear complexes of Ni(II) with other multidentate ligands.
- V. To study the kinetics of some bis and binuclear complexes of nickel(II) with some biologically important metal ions like  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  etc.
- VI. To carry out kinetic study of the reaction of some aminocarboxylato complexes of Iron(III) with  $\text{CN}^-$  ion.
- VII. To undertake kinetic study of the reaction of complexes of some macromolecules of Iron(III) with cyanide and other multidentate ligands.
- VIII. To explore the possibilities of using ligand substitution reactions as a kinetic tool for the determination of metal ions and ligands.

IX. Sometimes observation of solvent effects on the rate of reaction becomes a good tool for formulating a mechanistic scheme, particularly in the formation of ternary chelates, where solvent plays a vital role in the formation of an outer-sphere complex and its exchange with an incoming ligand. It is proposed to study the formation of ternary complexes between binary nickel(polyamine) complexes and Par in different solvent media viz.  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , DMSO, and DMF etc. to give further support for the hypothesis proposed so far.

X. To investigate some exchange reactions on aminocarboxylato ruthenium(III) complexes with  $\text{CN}^-$  ion to compare their behavior with the reaction of metal chelates studied earlier.

